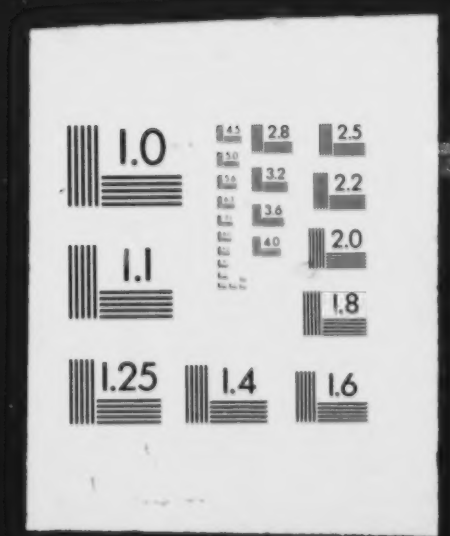


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SUMMARY OF EMISSIONS  
ASSOCIATED WITH PROPYLENE OXIDE

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY  
Office of Air and Radiation  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711

November 1988

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# CONVERSION FACTORS AND ABBREVIATIONS

| Symbol | Prefix or name | Factor by which unit is multiplied |
|--------|----------------|------------------------------------|
| G      | giga           | $10^9$                             |
| M      | mega           | $10^6$                             |
| mil    | million        | $10^6$                             |
| k      | kilo           | $10^3$                             |
| c      | centi          | $10^{-2}$                          |

## Units of length, area, and volume

$$1 \text{ m} = 3.28 \text{ ft.} = 1.09 \text{ yd.}$$

$$1 \text{ cm} = 0.394 \text{ in.}$$

$$1 \text{ m}^2 = 10.76 \text{ ft}^2$$

$$1 \text{ m}^3 = 35.31 \text{ ft}^3 = 264.2 \text{ U.S. gal}$$

## Units of mass

$$1 \text{ lb} = .4536 \text{ kg}$$

$$1 \text{ mil. lb} = .4536 \text{ Gy}$$

$$1 \text{ ton} = 2,000 \text{ lb}$$

## Units of pressure

$$1 \text{ atm} = 760 \text{ mm Hg} = 101,325 \text{ Pa}$$

$$1 \text{ kPa} = 9.87 \times 10^{-3} \text{ atm} = 0.145 \text{ psi}$$

## Units of temperature

$$x^{\circ}\text{F} = (y^{\circ}\text{C})(9/5) + 32$$

$$z \text{ K} = 273.15 + y^{\circ}\text{C}$$

## Ambient Conditions

$$1 \text{ atm, } 20\text{--}25^{\circ}\text{C}$$

| Abbreviation | Unit                   |
|--------------|------------------------|
| atm          | atmosphere             |
| ft           | foot                   |
| g            | gram                   |
| gal          | gallon                 |
| in           | inch                   |
| lb           | pound                  |
| m            | meter                  |
| Pa           | Pascal                 |
| psi          | pounds per square inch |
| yd           | yard                   |

| Symbol | Definition       |
|--------|------------------|
| R      | Organic compound |
| Hg     | Mercury          |
| Wt     | Weight           |

## 1. PROPYLENE OXIDE CHARACTERISTICS

Propylene oxide,  $\text{CH}_2\text{-}\overset{\text{O}}{\text{CHCH}_3}$ , is a highly flammable, low boiling liquid at ambient conditions. Because of its asymmetry, this chemical exists as two optical isomers. It is produced and used commercially as a mixture of these isomers.<sup>1,2</sup>

### 1.1. Physical Properties

Propylene oxide is soluble with most organic solvents.<sup>3</sup> It is only partially soluble in water and forms a two-layer aqueous system. At 25°C, the upper layer is 90 weight (wt) percent propylene oxide; the lower layer, 45 wt percent.<sup>2</sup>

Table 1-1 lists alternative names and various properties of this chemical.

Table 1-1 Chemical and Physical Properties of Propylene Oxide

O     H

Basic Structure: H - C - C - C - H

H   H   H

Alternative names: 1,2 epoxyp propane; methyloxirane; propene oxide

Chemical Abstract Service (CAS) Registry Number: 75-56-9

| <u>Property</u>  | <u>Value</u>           | <u>Conditions</u>        | <u>Reference</u> |
|------------------|------------------------|--------------------------|------------------|
| Molecular weight | 58.08                  |                          | 4                |
| Weight           | 6.9 lb/gal             | 20°C                     | 5                |
| Density          | .830 g/cm <sup>3</sup> | 20°C                     | 3                |
| Freezing Point   | -112°C                 |                          | 3                |
| Boiling Point    | 34.2°C                 | 101.3 kPa<br>(760 mm Hg) | 3                |
| Vapor Pressure   | 445 mm Hg              | 20°C                     | 5                |
|                  | 538 mm Hg              | 25°C                     | 1                |
| Explosive Limits | 2.3 to 37 volume %     | in air                   | 3                |
| Solubility       | partial                | in water                 | 5                |
|                  | complete               | in alcohol               | 5                |
|                  | complete               | in ether                 | 5                |

## 1.2 REACTIONS

Propylene Oxide is a very reactive chemical. Its reactivity is the result of the highly strained three-member ring geometry.<sup>1</sup> The characteristic epoxide ring ( $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -\text{C}-\text{C}- \end{array}$ ) can undergo cleavage catalyzed by acids or bases. Reactions with water, ammonia, amines, carbon dioxide, alcohols, and phenols and polymerization all have industrial applications.<sup>6</sup>

A chemical homologue of propylene oxide is ethylene oxide, ( $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$ ). These two chemicals react in similar ways based upon the epoxide rings, and have some similar uses.

### 1.3 REFERENCES

1. Boggy, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA-560/11-80-005. March 1980. p.2, 4, 5.
2. Hancock, E.G., ed. Propylene and Its Industrial Derivatives. New York, NY, John Wiley and Sons. 1973. p.273, 274.
3. Grayson, M., ed. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, Vol 19. New York, NY, John Wiley and Sons. 1982. p. 247, 248.
4. Weast, R.C., ed. The CRC Handbook of Chemistry and Physics, 60th edition. Boca Raton, FL. CRC Press. 1979. p.C-448.
5. Hawley, G.G., ed. The Condensed Chemical Dictionary. 10th edition. New York, NY. Van Nostrand Reinhold Company. 1981.
6. Morrison, R.T. and R.N. Boyd. Organic Chemistry, 3rd edition. Boston, MA. Allyn and Bacon, Inc. 1973. p.564-565.

## 2. PROPYLENE OXIDE PRODUCTION

### 2.1 INDIRECT

While the direct production of propylene oxide is readily identified as a source of propylene oxide emissions, it is also necessary to consider other sources of emissions. Fuel combustion can be an indirect source of propylene oxide.

Propylene oxide was found to be a product of the combustion of n-pentane,<sup>1</sup> and the combustion of n-hexane.<sup>2</sup> These studies did not measure the amount of propylene oxide produced. One reference estimated that the total quantities of ethylene oxide and propylene oxide emitted by these sources could approach millions of pounds.<sup>3</sup> The sources of hydrocarbon combustion include automobiles and large stationary sources.

Other indirect sources of propylene oxide have been mentioned in the literature. It is possible that epoxides are formed during the photochemical smog cycle.<sup>3</sup> In a study to assess the toxic hazard from thermally stressed polymers, propylene oxide was among the eluted compound from a heated polyurethane coated wire.<sup>4</sup>

Because of the high reactivity of propylene oxide, it is unlikely that propylene oxide is an unintentional by-product in other industrial processes or a contaminant in some other final product.<sup>3</sup> That is, even if it were produced in very small quantities it would probably undergo another reaction quickly and form a different compound such as propylene glycol.

While it is necessary to keep in mind all possible sources of propylene oxide, in the judgement of the author, the available literature and monitoring data do not support the claim (in reference 3) that propylene oxide is indirectly produced in significant amounts.

## 2.2 COMMERCIAL

Propylene oxide is produced at four sites in the United States. All of these sites are located along the Texas-Louisiana Gulf Coast near propylene supplies.<sup>5</sup> Two of these facilities manufacture propylene oxide using the chlorohydrin method. The other two facilities use the peroxidation method of manufacture.<sup>5,6</sup>

Ethylene oxide can be manufactured through the direct oxidation of ethylene. Although patents have been issued for direct oxidation of propylene, none of these processes have been found commercially feasible. Low yields, low raw material conversion, numerous by-products from complex catalyst systems and preferential attack of the methyl group, which results in acroliene,  $\text{CH}_2=\text{CHCHO}$ , are all problems arising in the direct oxidation methods of propylene oxide.<sup>5,7</sup>

Propylene, a colorless gas, is a raw material for the chlorohydrination and peroxidation processes. The oxidation of propylene to propylene oxide is an exothermic reaction and may produce significant quantities of heat.<sup>8</sup>

Brief descriptions of both of these processes follow. Detailed descriptions of these processes are available elsewhere.<sup>7,8,9,10</sup>

### 2.2.1 Chlorohydrination

The chlorohydrination of propylene to propylene oxide is a two-step process. In the first step, propylene, chlorine and an excess amount of water are in aqueous solution at, or slightly above atmospheric pressure and near  $45^\circ\text{C}$ . The chlorine and water form hydrochloric acid. This acid reacts with the propylene to form propylene chlorohydrin. Maintaining a dilute solution, i.e. 5 wt percent propylene chlorohydrin, helps to keep formation of by-products to a minimum in this step.<sup>5,7,8,10</sup>

In the second step, the chlorohydrin reacts with a base, to form propylene oxide and a salt. The base used is lime or caustic soda. The resulting salt is calcium chloride or sodium chloride. This reaction occurs at an elevated temperature under slight pressure so that the propylene oxide is vaporized as it is generated.<sup>8</sup>

The crude product stream is distilled under vacuum to reduce the hydrolysis of propylene oxide to propylene glycol. The composition of a crude product stream is given in Table 2-1.

Table 2-1 Crude Product Stream Composition\*

| <u>Component</u>     | <u>Estimated Weight Percent</u> |
|----------------------|---------------------------------|
| Water                | 70                              |
| Propylene oxide      | 26                              |
| Propylene dichloride | 3                               |
| Other compounds      | 1                               |

\*Grayson, M.ed, Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, vol. 19, New York, John Wiley and Sons, 1982.p.256.

One of the major drawbacks of this process is the large amount of by-products and waste materials that can be generated. Table 2-2 lists estimated amounts of feed, product and by-product. Recycle and sale of the generated salts is hindered by high energy costs. Research has been done in this area<sup>12</sup> but no evidence found during this study indicated that such processes have been commercialized.

Table 2-2 Relative Quantities of Feed, Product and By-product<sup>a,b</sup>

|              |                        |        |
|--------------|------------------------|--------|
| Feed:        | propylene              | 90 kg  |
| Product:     | propylene oxide        | 100 kg |
| By-products: | propylene dichloride   | 9 kg   |
|              | dichloropropyl ethers  | 2 kg   |
|              | calcium chloride brine | 215 kg |

- a. Peterson, C.A. (IT Enviroscience) Propylene Oxide Product Report. In: Organic Chemical Manufacturing, Volume 10: Selected Processes. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, NC. EPA-450/3-80-028e. December 1980.
- b. Boggy, D.A., S.S. Lande, W.A. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA-560/11-80-005. March 1980. p.26-28.

### 2.2.2 Peroxidation

In 1986, two facilities were using the peroxidation method to produce propylene oxide. In these facilities, an organic hydroperoxide is used to epoxidize propylene.<sup>5</sup> Propylene oxide is a co-product with tertiary alcohol or styrene. The reactions for this process are:



a. peroxidation of organic



b. oxidation of propylene

#### Peroxidation, t-butyl alcohol coproduct

In this process, the first step is the air oxidation of isobutane in the liquid phase to tertiary-butyl hydroperoxide.<sup>3</sup> Some tertiary-butyl alcohol is already formed at this step. In the next step, the propylene is introduced and metal, e.g. molybdenum, catalyzes the production of propylene oxide and t-butyl alcohol. This reaction usually occurs at 80-130°C and 1.8-7 MPa(250-1000 psig).<sup>5</sup> Finally, the products are separated and purified.

The stoichiometric minimum ratio of coproducts is 1.28 lb of t-butyl alcohol per lb of propylene oxide. The actual weight ratio is 3 lb t-butyl alcohol per lb propylene oxide.<sup>11</sup>

#### Peroxidation, styrene coproduct

Ethyl benzene is the organic chemical that is peroxidized in this process. The products of this first step are ethyl benzene hydroperoxide, methyl benzyl alcohol, and acetophenone. A metal such as molybdenum or titanium is used in a soluble metal catalyst system to catalyze the ethyl benzene hydroperoxide and propylene. This produces propylene oxide and alpha-methyl benzyl alcohol. The propylene oxide is separated and distilled. The alpha-methyl benzyl alcohol is dehydrated to styrene.<sup>5</sup>

The stoichiometric minimum ratio of coproducts is 1.79 lb styrene to 1 lb propylene oxide. The actual ratio is 2.5 lb styrene to 1 lb propylene oxide.<sup>11</sup>

## 2.3 REFERENCES

1. Barnard, J.A. and RKY Lee. Combustion of n-pentane in a schock tube. *Combustion Science and Technology*. 6(3):143-150. 1972.
2. Hughes, K.J., R.W. Hurn, and F.G. Edwards. Separation and Identification of Oxygenated Hydrocarbons in Combustion Products from Automotive Engines. In: *International Symposium on Gas Chromatography* (2nd, 1959; Michigan State University). New York, NY. Academic Press. 1961. p.171-182.
3. Bogyo, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA-560/11-80-U05. March 1980. p.12,26-28,30,67,68.
4. Rigby, L.J. The Collection and Identification of Toxic Volatiles from Plastics under Thermal Stress. *Ann. Occup. Hyg. (United Kingdom)*. 24(4):331-345. 1981.
5. Grayson, M., ed. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Vol 19. New York, NY. John Wiley and Sons, 1982. p.249-258,262,263.
6. SRI International. 1985 Directory of Chemical Producers. Menlo Park, CA. 1985. p.844.
7. Hancock, E.G., ed. *Propylene and Its Industrial Derivatives*. New York, NY. John Wiley and Sons. 1973. p.276-279.
8. Peterson, C.A. (IT Envirosience) Propylene Oxide Product Report. In: *Organic Chemical Manufacturing, Volume 10: Selected Processes*. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, NC. EPA-450/3-80-U28e. December 1980. p.III-1, III-3-III20.
9. Hydrosience, Inc. Trip Report to Oxirane, Channelview, TX, October 18, 1978. In: *Hydrosience files, Emission Standards and Engineering Divison*, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC.
10. Hydrosience, Inc. Trip Report to Dow, Plaquemine, LA. November 16-17, 1977. In: *Hydrosience Files, Emission Standards and Engineering Division*, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC.
11. Mannsville Chemical Products Corporation. *Chemical Products Synopsis: Propylene Oxide*. Cortland, NY. February 1984.
12. Propylene Oxide puts its Waste to Work. *Chemical Week*. April 5, 1978. p.33-34.

### 3.0 PROPYLENE OXIDE USES

Propylene oxide was the 40th highest volume chemical produced in 1979.<sup>1</sup> In 1987, propylene oxide had the 38th highest production volume.<sup>53</sup> Its primary function is that of a chemical intermediate in the manufacture of other chemical compounds. Most of the propylene oxide produced is used to manufacture polyether polyols for use in urethane foams, functional fluids and surface-active agents (surfactants). Another major derivative of propylene oxide is propylene glycols and the associated dipropylene and tripropylene glycols. Propylene oxide is used to manufacture glycol ethers, isopropanol amines, nonpolyolbased surfactants, and propylene carbonate. Approximately 170 Mg per year, or 0.02 percent of total annual production of propylene oxide is used as a fumigant or a sterilant.<sup>1,2</sup>

It should be noted that the categories of use for propylene oxide are not clearly defined. For example, polypropylene glycol might be considered to be in the category of polyether polyols for non-urethane applications. It might also be considered part of the propylene glycol category or even in the miscellaneous category. The existence of this ambiguity is most significant for the production estimates of the emission source categories. (see Appendix G).

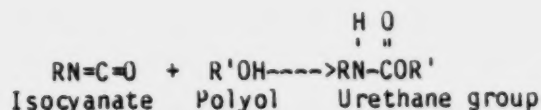
### 3.1 POLYETHER POLYOLS

A polyol is the product of a reaction between an epoxide and a compound which contains active hydrogens such as glycols, amines, acids or water.

Polyether polyols are polymers with the characteristic ether linkage (R-O-R) which are based upon tri- or polyhydric alcohols. A compound with two hydroxyl groups (-OH) is commonly referred to as a diol. A polyol has three or more hydroxyl groups.<sup>3</sup> The molecular weight of a polyol can range from 200 to 7,000.<sup>4</sup>

#### 3.1.1 Urethane Applications

The production of polyether polyols for urethane applications is the largest use category for propylene oxide. The basic reaction is shown below.



Polyol, Isocyanate Reaction<sup>3,5</sup>

The hydrogen atom that becomes attached to the nitrogen is active and may provide a reactive point for additional crosslinking. Isocyanates react with water to form an amine and carbon dioxide. This reaction can be used to cause foaming while polymerization continues. In this manner, flexible and rigid polyurethane foams can be manufactured.

Flexible and semiflexible foams are used in furniture, transportation, rugs and underlays, bedding, packaging and textile laminates. Of the total domestic consumption of polyether polyols for urethane applications, 74 percent was used for flexible foams in 1979.<sup>7</sup>

Rigid foams are manufactured using lower ratios of polyol to isocyanate. These foams form the second largest urethane usage group. They are used in building construction, appliances, packaging, transportation, furniture and marine flotation.<sup>5</sup>

Urethane foams are usually manufactured in a one-shot process. That is, all raw materials are combined in a single step.<sup>7</sup>

The urethane reaction can also be used for nonfoam products. These can be microcellular or noncellular. Nonfoam uses include surface coatings, elastomers, fibers and thermosetting resins.<sup>13</sup> Elastomers may be manufactured by mixing the polyols and isocyanates and then pouring or injecting them into the mold. They may also be manufactured by reaction-injection molding (RIM) in which the feedstreams are separately metered to a mixing head, then injected directly into the mold.<sup>7</sup> Elastomers are used for shoe uppers and heels, encapsulating electronic parts, films, linings, and adhesives.<sup>1</sup>

### 3.1.2 Non-Urethane Applications

Polyether polyols are also used in non-urethane applications. Approximately 40 percent of these polyols are used as surface active agents (surfactants). Surfactant polyols may be used as dispersants, defoamers, oil-field chemicals, such as crude oil demulsifiers, power transmission fluids, lubricants, greases, and wetting agents.<sup>7</sup> These polyols can be in the configuration of random or block copolymers of polypropylene glycol and polyethylene glycol.

Another 40 percent of these polyether polyols are used as lubricants and functional fluids. The remaining 20 percent are used in pharmaceuticals, cosmetics, toiletries, and the plasticizer industries.<sup>8,9</sup>

### 3.2 PROPYLENE GLYCOLS

The source category "Propylene Glycols," includes propylene glycol dipropylene glycol (DPG), and tripropylene glycol (TPG). Propylene Glycol is considered nontoxic. It is classified as a generally recognized as safe (GRAS) chemical by the Food and Drug Administration.<sup>10</sup> This non-toxicity allows it to be used in a variety of pharmaceutical, cosmetic, food, and drug processes and formulas. Propylene glycol is primarily used to produce unsaturated thermoset polyester resins. Propylene glycol is also used in antifreezes, hydraulic fluids, pet foods, functional fluids (including heat transfer fluids and brake fluids), paints and coatings, plasticizers, and as a tobacco humectant and cellophane softening agent.<sup>8</sup> Dipropylene glycol is used in hydraulic fluids, cutting oils, textile lubricants, ink formulations, industrial soaps, and solvents and it is an indirect food additive.<sup>11</sup> Tripropylene glycol is used in cleansing creams, textile soaps, lubricants, and cutting oil concentrates.<sup>4</sup>

DPG and TPG are coproducts of propylene glycols. The relative capacity for these three glycols can be manipulated by the reaction conditions but they are usually present as 10 percent and 1 percent (respectively for DPG and TPG) of the propylene glycol product.<sup>8</sup>

Propylene glycol is produced under pressure, at temperatures up to 200°C, without a catalyst, by reacting 15-20 moles of water for every mole of propylene oxide.<sup>3,4</sup> The reaction is carried out in a jacketed pipe system. Water and propylene oxide are added and the dilute mixed glycol solution is withdrawn at a rate that will maintain a constant composition along the pipe. The product is dehydrated in a vacuum evaporator and the glycols are separated in a multicolumn distillation system.<sup>3</sup> Approximately 0.8 lb propylene oxide are consumed for each pound of propylene glycol produced.<sup>7</sup>

Propylene glycol is easily biodegraded by many micro-organisms. In fresh water or salt water, 55 percent or more of the original propylene glycol is bio-oxidized after 5 days.<sup>10</sup>

### 3.3 GLYCOL ETHERS

Glycol ethers are obtained from the reaction of an epoxide and an alcohol or phenol.<sup>4</sup> They are used primarily in formulations of mixed solvents for paints, resins and inks.<sup>3</sup> Glycol ethers are miscible in water so they can be used in aqueous solvent systems. Glycol ethers are also used as synthetic lubricants, hydraulic and automotive brake fluids, coupling agents, and heat transfer fluids.<sup>4</sup>

Specific chemical names for some widely used glycol ethers are listed in Table 3-1.

Table 3-1 Names of Glycol Ethers\*

| <u>Common Name</u>                   | <u>Chemical Name</u>                      |
|--------------------------------------|-------------------------------------------|
| Propylene Glycol Monomethyl Ether    | 1 methoxy-2-propanol                      |
| Dipropylene Glycol Monomethyl Ether  | 3-(3-methoxypropoxy) propanol             |
| Tripropylene Glycol Monomethyl Ether | 3-(3-(3-methoxypropoxy) propoxy) propanol |

\* SRI International. Chemical Economics Handbook. Menlo Park, CA. 1978-1980. p.690.8022T.

### 3.4 MISCELLANEOUS

Propylene oxide is used to produce a variety of chemicals other than polyether polyols, propylene glycols and glycol ethers. These chemicals include isopropanolamines, propylene carbonate, polypropylene glycol, and nonpolyol based surfactants. Some propylene oxide is used directly as a sterilant or fumigant for food and other products.<sup>9</sup>

#### 3.4.1 Isopropanolamines

Isopropanolamines, 1-amino-2-propanols, are the result of the reaction of propylene oxide, ammonia, and water.<sup>4</sup> These products can react chemically as both amines and alcohols. They are used with fatty acids in emulsifiers, detergents, foam stabilizers and shampoos.

Although propylene oxide and ammonia can react spontaneously at room temperature, the industrial process usually occurs in a tube reactor with aqueous ammonia at temperatures up to 100°C and pressures up to 300 psi.<sup>3</sup> An estimated 10-15 million lbs of propylene oxide were consumed in 1979 to produce mono-, di-, and tripropanolamines.<sup>8</sup>

#### 3.4.2 Propylene Carbonate

Propylene carbonate is manufactured by reacting propylene oxide with carbon dioxide. It is used as a solvent for organic and inorganic gases and as a gas conditioner for removal of hydrogen sulfide, carbon dioxide, and mercaptans. An estimated 2 million lbs of propylene oxide were consumed for this use in 1979.<sup>4,8</sup>

#### 3.4.3 Nonpolyol based Surfactants

Surface active agents, surfactants, which are not based upon polyether polyols provide another market for the consumption of propylene oxide. Table 3-2 gives specific examples of these chemicals. These surfactants are usually propoxylated compounds.

Mixed linear propoxylated alcohols is the most significant of these compounds. Propylene oxide/ethylene oxide block copolymer surfactants are used as crude oil demulsifiers and for breaking water-in-oil emulsions.<sup>9</sup>

Table 3-2 Nonpolyol based Surfactants\*

| <u>Type</u> | <u>Characteristics</u>                                                | <u>Example</u>                                                         |
|-------------|-----------------------------------------------------------------------|------------------------------------------------------------------------|
| Amphoteric  | anionic or cationic<br>notable for mildness<br>personal care products | oleic acid-ethylenediamine<br>condensate, propoxylated,<br>sodium salt |
| Anionic     | positive charge<br>disinfectant,<br>fabric softener                   | hexyloxy propyl sulfate,<br>sodium salt                                |
| Cationic    | negative charge<br>high sudsing                                       | [coconut oil alkyl]amine,<br>propoxylated                              |
| Nonionic    | contains neither anions<br>nor cations<br>mild, low sudsing           | mixed linear alcohols,<br>ethoxylated and propoxylated                 |

\*SRI International. Chemical Economics Handbook. Menlo Park, CA. 1978-1980 editions. p.690.8022 U.

#### 3.4.4 Fumigant/Sterilant

Although the use of propylene oxide for fumigation does not consume large amounts of propylene oxide, this minor use category is of special interest because of a number of considerations. When used as a fumigant, unless emission control devices are used at the facility, all of the propylene oxide consumed will probably be emitted to the atmosphere. The propylene oxide which remains in the food product might react to form propylene glycol or it might form propylene chlorohydrin. The Food and Drug Administration (FDA) regulates the amounts of residues that can remain in foods that are designated for consumption.

Propylene oxide has been studied for use as a sterilant for therapeutic immunoadsorbents.<sup>12</sup> The sterilization use may allow some replacement of ethylene oxide which is generally the preferred sterilant. Propylene oxide is less toxic than ethylene oxide but it is also substantially less antimicrobial.

Because of the greater toxicity of ethylene oxide, propylene oxide has been considered as an alternative fumigant. Use of propylene oxide is limited by the necessity of heating it to 35°C (95°F) to reach the gaseous phase. This heating can reduce the quality of some products, such as spices.<sup>13</sup> It also makes the residues more difficult to remove. During the fumigation of a few foods, e.g. cocoa beans, propylene oxide is preferentially used because ethylene oxide causes quality deterioration.

Propylene oxide is allowed by the FDA as a package fumigant for dried prunes and glace fruit. A residue of 700 ppm propylene glycol is allowed. Propylene oxide is also allowed as a bulk fumigant for foods such as cocoa, gums, spices, starch and nutmeats (except peanuts) that are to be further processed. The residue limit is 300 ppm of propylene oxide. Propylene oxide can also be used in modified food starch. Residue is limited to 5 ppm of propylene chlorohydrin.<sup>14</sup>

Residues of the epoxides, propylene oxide and ethylene oxide, have been studied.<sup>15</sup> The propylene oxide combines with the elements of water to form propylene glycols or it combines with the elements of hydrochloric acid to form propylene chlorohydrin.<sup>16</sup> One reference estimated that the intake of as much as 21 mg of propylene chlorohydrin can result from the fumigation of 1 lb of food.\*

\*Reference 17. The calculations that obtained this result were not included in the paper. It should also be noted that the calculations were made in 1975 and were probably made without regard to U.S. FDA regulations as it was not a domestic study.

Residual propylene oxide has been found on fumigated foods in other studies. Various plastics and cellulose products used as food wrappings and containers also have been found to contain propylene oxide residue. 6,18,19

#### 3.4.5 Other

Propylene oxide was used as a raw material for the production of glycerin, but this Bayport, Texas, plant was shut down by FMC in 1982.<sup>7</sup>

Propylene oxide is a stabilizer for fuel and heating oils, methylene chloride, and vinyl resin lacquers. It is a solvent for various resins, commercial gums, hydrocarbons, and cellulose derivatives.<sup>11</sup>

Besides being used as an intermediate chemical, propylene oxide can also be used as a process chemical, that is, not used directly as an ingredient of the final product but used to facilitate or catalyze the necessary reactions. 20,21

### 3.5 REFERENCES

1. Hawley, G.G., ed. The Condensed Chemical Dictionary, 10th edition, New York, NY. Van Nostrand Reinhold Company. 1981. p.839, 840, 865.
2. Windholz, M., ed. The Merck Index, 10th edition. Rayway, New Jersey, Merck and Company, Inc. 1983, p.7764.
3. Hancock, E. G., ed. Propylene and Its Industrial Derivatives. New York NY, John Wiley and Sons. 1973. p.287,288,292-295.
4. Grayson, M., ed. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition. Vol 19. New York, NY. John Wiley and Sons, 1982. p.249-251, 264,267,268.
5. Considine, D.M., ed. Chemical and Process Technology Encyclopedia. New York, NY. McGraw Hill Book Company. 1974. p.1121.
6. Society of the Plastics Industry (SPI). Quarterly Polyols and Isocyanates Reports. In: Facts and Figures of the U.S. Plastics Industry, 1985 ed. New York, NY. p.31,50,51.
7. Mannsville Chemical Products Corporation. Chemical Products Synopsis: Propylene Oxide. Cortland, New York. February 1984.
8. SRI International. Chemical Economics Handbook. Menlo Park, CA. 1978-1980. p.688.3500A, 690.6050C, J, 690.8022U.
9. Bogyo, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA 560/11-80-005. March 1980. p.46.
10. Miller, L.M. Investigation of Selected Potential Environmental Contaminants: Ethylene Glycol, Propylene Glycols, and Butylene Glycols. U.S. Environmental Protection Agency. Washington, D.C. EPA-560/11-79-006. May 1979, p.i, 62,63.
11. Occupational Health Guidelines for Propylene Oxide. National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services and Occupational Safety and Health Administration, U.S. Department of Labor. Washington, D.C. September 1978.
12. Sato, H., T. Kidaka, and M. Hori. The Sterilization of Therapeutic Immunoabsorbents with Aqueous Propylene Oxide Solution. Inter. T. Artif. Organs. 8(2):109-14. 1985.

13. Memorandum from Beloian, A., Benefits and Use Division, Office of Pesticides and Toxic Substances (OPTS), U.S. EPA to Lapsley, P. Special Review Branch Registration Division. OPTS, USEPA. June 11, 1985. Ethylene Oxide: Nonmedical uses.
14. Food Chemical News, Inc. The Food Chemical News Guide. June 28, 1982. p.374.1,374.2.
15. Lindgren, D.L., W.B. Sinclair, and L.E. Vincent. Residues in raw and processed foods resulting from post-harvest insecticidal treatment. Residue Reviews. 21:93-95. 1968.
16. Wesley, F., B. Rourke, and O. Darbishire. The Formation of persistent toxic chlorohydrins in foodstuffs by fumigation with ethylene oxide and with propylene oxide. Journal of Food Science. 30: 1037-1042. 1965.
17. Rosenkranz, H.S., T.J. Wlodkowski, and S.R. Bodine. "Chloropropanol, a Mutagenic Residue Resulting from Propylene Oxide Sterilization. Mutation Research 30:303-304.1975.
18. International Agency for Research on Cancer (IARC), World Health Organization. Propylene Oxide. In: Cadmium, Nickle, Some Epoxides, Miscellaneous Chemicals, and General Considerations on Volatile Anaesthetics. Lyon, France. 11:191-199. 1976.
19. Kereluk, K., Propylene Oxide. In: Gaseous Sterilization: Methylene Bromide, Propylene Oxide, and Ozone. Prog. Inc. Microbiol. 10:117-125. 1971.
20. Large, G.B. and Buren, L.L. Phosphonium Salts of N-phosphonomethylglycine and their use as herbicides and plant growth regulators. Patent pending. U.S. Application No. 295345 (810824) or 374539 (820505).
21. Chemical and Engineering News, Top 50 Chemicals Production Turned Back Up in 1987. Vol.66, no. 15, April 11, 1988. p.31.

## 4. INDUSTRIAL GROWTH

### 4.1 HISTORY

Propylene oxide was first identified in 1860. It was first manufactured in Germany during World War I. Propylene oxide became a major industrial chemical soon after World War II.<sup>1,2,3</sup>

The process used for production was the chlorohydrin process. This process was also used for production of ethylene oxide. Around 1940, Union Carbide Corporation began producing ethylene oxide by direct oxidation. The direct oxidation of ethylene oxide gradually became the preferred process for production of ethylene oxide. This made available chlorohydrin plants which could be easily converted to the production of propylene oxide.<sup>1,4</sup>

In the 1960's, propylene oxide demand increased 15 percent per year, from 1970-1979, demand increased 7 percent per year.<sup>3</sup>

In 1968, Atlantic Richfield Corporation (ARCO) and Halcon International formed Oxirane and commercialized the hydroperoxidation process for propylene oxide production. The isobutane peroxidation process was an economically competitive process and small producers who used the chlorohydrin process began dropping out of the market. In 1977, Oxirane's ethylbenzene peroxidation plant came on line. The economics of the peroxidation process depend upon the coproduct markets as well as the propylene oxide market because of the large amount of coproducts produced.<sup>1,2,5</sup>

In 1980, ARCO purchased Halcon's share of the Oxirane facilities. In this same year, an economic recession began which reduced automobile production and housing starts. Propylene oxide consumption shrank 26 percent from 2.11 billion lbs in 1979 to 1.56 billion lbs in 1982.<sup>3</sup> The existence of the rival peroxidation process and the decreased demand for propylene oxide were contributing reasons for the remaining small producers to shut down their facilities.

Only Dow and ARCO, with two plants each, continued to produce propylene oxide for the years from 1983 to 1986. Propylene oxide demand has increased steadily during this time. These two companies remain the only domestic producers of propylene oxide.

## 4.2 OUTLOOK

Demand for propylene oxide is primarily dependent upon the demand for polyurethane polyols and propylene glycols. Demand for these products is dependent upon their end product markets, such as the transportation and construction markets.

Demand for the major consumers of propylene oxide will probably increase from 4 percent to 7 percent from 1984 to 1989. Propylene oxide production is expected to increase by approximately 4 percent per year during the same period.<sup>3</sup>

Production facilities are currently operating at 73 percent of capacity. (See Appendix B.) Additional demand is more likely to be satisfied by expansion of the Dow and ARCO facilities than by new plant startups.

#### 4.3 REFERENCES

1. Hancock, E.G., ed. Propylene and Its Industrial Derivatives. New York, NY. John Wiley and Sons. 1973. p.273,274,282.
2. Grayson, M., ed. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, Vol 19. New York, NY. John Wiley and Sons. 1982. p.253,257.
3. Mannsville Chemical Products Corporation. Chemical Products Synopsis: Propylene Oxide. Cortland, NY. February 1984.
4. Peterson, C.A. (IT Enviroscience). Propylene Oxide Product Report. In: Organic Chemical Manufacturing Volume 10: Selected Processes. Office of Air Quality Planning and Standards. U.S. EPA. Research Triangle Park, NC. EPA-450/3-80-028e. December 1980. p.III-2.
5. Bogoy, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. EPA. Washington, D.C. EPA-560/11-80-005. March 1980. p.30.

## 5. PROPYLENE OXIDE EMISSIONS

This section of the report contains emission estimates and related data for production and consumption facilities. Most of the emissions are annual averages. The only information available on short term, or peak emissions, is for use of propylene oxide as a fumigant at an Illinois facility. Further information and calculations regarding this usage can be found in Appendix J.

Some of the annual emission estimates in this report were calculated using emission factors. An emission factor is "an average value which relates the quantity of a pollutant released to the atmosphere with the activity associated with the release of that pollutant."<sup>1</sup> Emission factors used here relate the total annual quantity of emissions to the total annual quantity of propylene oxide or other chemical produced.

The emission factor for a process emission or emission point was given in other references or was based upon emission factors or emission rates given in other references. For example, a reference might give total VOC from a propylene oxide process unit, for the industry or at a specific facility. That total VOC could be divided by the total propylene oxide produced or consumed at the facility. The number would then be multiplied by an estimate or calculation of the propylene oxide fraction in the VOC. The resulting number is a propylene oxide emission factor for the process emissions.

The fugitive emissions, or equipment leaks, for those facilities were not determined using emission factors. Equipment leaks are not proportional to production volume. They are a function of the complexity of a process. In other words, the quantity of emissions from equipment leaks depends upon the number of process components, such as valves and pumps, that could leak. For most of the facilities, the size of a typical production unit and the ratio of propylene oxide to total VOC were based upon available data, such as process flow diagrams available in general references.

Depending upon the available data, different levels of error and uncertainty are present in the final estimates. The approximations and assumptions are chosen so that the emission estimates, and subsequent concentration estimates, will err by being too high, rather than too low. Applying this rule to calculations is referred to as choosing the conservative assumption.

The bases, calculations, assumptions, and references for specific emission estimates are given in the appendices.

### 5.1 Domestic Production, Consumption, Imports, and Exports

In 1986, an estimated 950 Gg (2100 mil lbs) of propylene oxide was produced in the U.S. Approximately 860 Gg (1900 mil lbs) is estimated to have been consumed. The amount of propylene oxide produced and consumed in recent years is given in Table 5.1-1

TABLE 5.1-1 PROPYLENE OXIDE SUPPLY AND DEMAND  
(millions of lbs)<sup>a</sup>

| Year       | 1981 | 1982 | 1983 | 1984              | 1985              | 1986              |
|------------|------|------|------|-------------------|-------------------|-------------------|
| Capacity   | 2760 | 2760 | 2860 | 2860              | 2870              | 2870              |
| Production | 1831 | 1660 | 1840 | 1900 <sup>c</sup> | 2000 <sup>c</sup> | 2100 <sup>c</sup> |
| Imports    | 89   | 51   | 32   | 26 <sup>b</sup>   | 30 <sup>c</sup>   | 30 <sup>c</sup>   |
| Exports    | 178  | 146  | 166  | 180 <sup>c</sup>  | 200 <sup>c</sup>  | 210 <sup>c</sup>  |
| Demand     | 1742 | 1565 | 1706 | 1750 <sup>c</sup> | 1800 <sup>c</sup> | 1900 <sup>c</sup> |

<sup>a</sup> Unless otherwise noted, values are from:  
Mannsville Chemical Products Corporation. Chemical Products  
Synopsis: Propylene Oxide. Cortland, NY. February 1984.

<sup>b</sup> Chemical Imports in 1984. Chemical Week. February 20, 1985. p.36.

<sup>c</sup> Estimated values. For method of calculation, see appendix A.

Propylene oxide is domestically produced at four facilities. There are 36 production sites for the manufacture of polyether polyols, the largest consumption category for propylene oxide. Table 5.1-2 indicates the number of companies and the number of major facilities for all the emission source categories.

TABLE 5.1-2 NUMBER OF MAJOR FACILITIES<sup>a</sup>

| <u>Source category</u> | <u>No. of companies</u> | <u>No. of facilities</u> |
|------------------------|-------------------------|--------------------------|
| Production             | 2                       | 4                        |
| Polyether Polyols      | 22                      | 36                       |
| Propylene Glycols      | 4                       | 5                        |
| Glycol Ethers          | 4                       | 7                        |

a. SRI International. 1985 Directory of Chemical Producers. Menlo Park, CA. 1985.

## 5.2 PRODUCTION FACILITIES

Based upon the total capacity and estimated total production, it was calculated that each facility would operate at 73 percent capacity. Production estimates for each site are given in Table 5.2-1. Appendix B contains calculations for this section.

TABLE 5.2-1 PRODUCTION ESTIMATES FOR MANUFACTURING FACILITIES

| Company | Location        | Process                      | 1986 Capacity <sup>a</sup><br>(mil lbs) | Estimated<br>1986 Production <sup>b</sup> |      |
|---------|-----------------|------------------------------|-----------------------------------------|-------------------------------------------|------|
|         |                 |                              |                                         | (mil lbs)                                 | (Gg) |
| ARCU    | Bayport, TX     | isobutane<br>peroxidation    | 1020                                    | 740                                       | 340  |
|         | Channelview, TX | ethylbenzene<br>peroxidation | 500                                     | 360                                       | 160  |
| Dow     | Freeport, TX    | chlorohydration              | 950                                     | 690                                       | 310  |
|         | Plaquemine, LA  | chlorohydration              | 400                                     | 290                                       | 130  |

<sup>a</sup> SRI International. 1985 Directory of Chemical Producers. Menlo Park, CA. 1985.

<sup>b</sup> See Appendix B for calculations

Emission estimates and emission stream characteristics which were developed in this source assessment, are appropriate for use in the Human Exposure Model (HEM).

The Human Exposure Model is a screening model which uses (1) emission estimates for point sources, (2) meteorological data for locations near these sources, (3) population data from the census, and (4) risk factors which are developed from health assessments for the specific chemical to calculate potential levels of exposure and estimate the number of people who might be exposed. HEM values for the production facilities are given in Table 5.2-2.

Notes concerning plant location data, zone characterization, and other information in the HEM input tables may be found in Appendix C. Appendix E contains information concerning the equipment leak emission estimates. Storage and transportation related emission estimates are treated in Appendix F.

TABLE 5.2-2 PROPYLENE OXIDE PRODUCERS  
HEM INPUTS<sup>a</sup>

| COMPANY<br>CITY,<br>STATE | LATITUDE<br>(° "N) | LONGITUDE<br>(° "W) | ZONE | PROCESS<br>IDENT.             | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>RELEASE<br>HEIGHT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs) |
|---------------------------|--------------------|---------------------|------|-------------------------------|---------------|--------------------------|---------------------------|--------------|-----------------------------------|-----------------------|------------------------|-----------------------|------------------------|----------------|
| ARCO,<br>Bayport, TX      | 29 39 08           | 95 01 52            | 1    | Perox<br>Reactor              | P             | 6,400                    | 500                       | 0            | 23.                               | .30                   | 1.5                    | 289                   | .20                    | 8,760          |
|                           |                    |                     |      | Perox<br>Condens.             | P             | 1,000                    | 500                       | 0            | 14.                               | .08                   | 17.                    | 294                   | .03                    | 8,760          |
|                           |                    |                     |      | Peroxid-<br>ation             | E             | 94,500                   | 45,000                    | 1            | 3.0                               | -----                 | .01                    | 300                   | 3.00                   | 8,760          |
|                           |                    |                     |      | Peroxid-<br>ation             | S             | 10,400                   | -----                     | 1            | 6.0                               | .03                   | .01                    | 300                   | .33                    | 8,760          |
| ARCO,<br>Channelview, TX  | 29 46 30           | 95 07 30            | 1    | Perox<br>Reactor              | P             | 3,100                    | 500                       | 0            | 23.                               | .30                   | 1.5                    | 289                   | .10                    | 8,760          |
|                           |                    |                     |      | Perox<br>Condens.             | P             | 500                      | 500                       | 0            | 14.                               | .08                   | 17.                    | 294                   | .02                    | 8,760          |
|                           |                    |                     |      | Peroxid-<br>ation             | E             | 94,500                   | 45,000                    | 1            | 3.0                               | -----                 | .01                    | 300                   | 3.00                   | 8,760          |
|                           |                    |                     |      | Peroxid-<br>ation             | S             | 5,100                    | -----                     | 1            | 6.0                               | .03                   | .01                    | 300                   | .16                    | 8,760          |
| DOW,<br>Freeport, TX      | 28 57 06           | 95 21 24            | 0    | Chlorohy-<br>dric<br>Reactor  | P             | 12,200                   | 500                       | 0            | 23.                               | .30                   | 1.5                    | 289                   | .39                    | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric<br>Condens. | P             | 5,000                    | 500                       | 0            | 14.                               | .08                   | 17.                    | 294                   | .07                    | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric             | E             | 94,500                   | 45,000                    | 1            | 3.                                | -----                 | .01                    | 300                   | 3.00                   | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric             | S             | 9,700                    | -----                     | 1            | 6.                                | .03                   | .01                    | 300                   | .31                    | 8,760          |
| DOW,<br>Plaquemine, LA    | 30 17 20           | 91 14 03            | 0    | Chlorohy-<br>dric<br>Reactor  | P             | 5,200                    | 500                       | 0            | 23.                               | .30                   | 1.5                    | 289                   | .16                    | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric<br>Condens. | P             | 2,100                    | 500                       | 0            | 14.                               | .08                   | 17.                    | 294                   | .07                    | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric             | E             | 94,500                   | 45,000                    | 1            | 3.                                | -----                 | .01                    | 300                   | 3.00                   | 8,760          |
|                           |                    |                     |      | Chlorohy-<br>dric             | S             | 4,100                    | -----                     | 1            | 6.                                | .03                   | .01                    | 300                   | .13                    | 8,760          |

<sup>a</sup> Appendix C contains explanations of the fields in the table.

### 5.3. USER FACILITIES

It was necessary to estimate the amount of propylene oxide which would be consumed in 1986 by each major source categories. The calculations and assumptions used to determine these estimates can be found in Appendix G. The results are displayed in Table 5.3-1.

TABLE 5.3-1 PROPYLENE OXIDE CONSUMPTION ESTIMATES  
1986 DOMESTIC CONSUMPTION

|                                                           | (%) | (mil lbs) | (Gg) |
|-----------------------------------------------------------|-----|-----------|------|
| Polyether Polyols for Urethane Applications               | 56  | 1,050     | 480  |
| Polyether Polyols for non-Urethane applications           | 11  | 200       | 100  |
| Propylene Glycol, Dipropylene Glycol, Tripropylene Glycol | 24  | 450       | 210  |
| Glycol Ethers                                             | 1   | 20        | 10   |
| Miscellaneous uses                                        | 8   | 150       | 70   |

Capacity estimates for specific facilities in 1985 were available.<sup>6</sup> These capacities were used to prorate the total consumption for each source category to give an estimate of the propylene oxide usage at each facility.

Occasionally, capacities were given as a company total for two or more sites. In these cases, it was assumed that the capacities of all facilities were equal.

### 5.3.1 Polyether Polyols

The emission factors for propylene oxide in the production of polyether polyols were assumed to be the same for urethane and non-urethane polyols. This assumption was necessary because no other data were available.

#### 5.3.1.1 Urethane Applications

Table 5.3.1-1 lists the 1985 capacities and the estimated 1986 consumption values for facilities which manufacture polyether polyols for urethane applications. The emission estimates for these facilities are also given in the table. Appendices D, E, F, and H contain pertinent values and calculations.

#### 5.3.1.2 Non-Urethane Applications

Estimated 1986 consumption values and emission estimates for non-urethane polyether polyol facilities are given in Table 5.3.1-2.

TABLE 5.3.1-1 POLYETHER POLYOLS FOR URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE                        | LATITUDE<br>(° N) | LONGITUDE<br>(° W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS,<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985<br>capa-<br>city <sup>a</sup><br>(mil.<br>of lbs) | 1986<br>consum-<br>tion<br>P.O. ( |
|---------------------------------------------------|-------------------|--------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|--------------------------------------------------------|-----------------------------------|
| BASF,<br>Geismar,<br>LA                           | 30 12 12          | 91 01 24           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 5,600<br>8,100<br>400        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .18<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 200                                                    | 43                                |
| BASF,<br>Washington,<br>NJ                        | 40 45 30          | 75 58 54           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 2,200<br>8,100<br>200        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .07<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 80                                                     | 17                                |
| BASF,<br>Wyandotte,<br>MI                         | 42 12 00          | 83 09 00           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 6,200<br>8,100<br>500        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .20<br>.26<br>.02      | 8,760<br>8,760<br>8,760 | 225                                                    | 48                                |
| CARPENTER,<br>Bayport,<br>TX                      | 29 39 08          | 95 01 52           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 6,100<br>8,100<br>500        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .19<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 220                                                    | 47                                |
| DOW,<br>Freeport,<br>TX                           | 28 57 06          | 95 21 24           | 0    | Polyether<br>Polyols | P<br>E<br>S   | 11,000<br>8,100<br>800       | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .35<br>.26<br>.03      | 8,760<br>8,760<br>8,760 | 400                                                    | 8 <sup>a</sup>                    |
| MINNESOTA<br>MINING AND<br>MFG.<br>Decatur,<br>AL | 34 36 12          | 86 58 42           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>8,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.26<br>.001     | 8,760<br>8,760<br>8,760 | 15                                                     | 5                                 |

<sup>a</sup> Reference 7.

TABLE 5.3.1-1 POLYETHER POLYOLS FOR URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE         | LATITUDE<br>(°' "N) | LONGITUDE<br>(°' "W) | ZONE | PROCESS<br>TUDENT.   | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT (m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985<br>capa-<br>city<br>(mil.<br>of lbs) | 1986 est.<br>consump-<br>tion of<br>P.O. (Gg) |
|------------------------------------|---------------------|----------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|-------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|-------------------------------------------|-----------------------------------------------|
| MOBAY<br>Cedar Bayou,<br>TX        | 29 44 00            | 94 56 30             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 4,300<br>8,100<br>330        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .14<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 155                                       | 33.                                           |
| MOBAY<br>New Martins-<br>ville, WV | 39 38 36            | 80 51 36             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 2,000<br>8,100<br>200        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .06<br>.26<br>.005     | 8,760<br>8,760<br>8,760 | 70                                        | 15.                                           |
| OLIN,<br>Brandenburg,<br>KY        | 38 00 00            | 86 10 12             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 6,100<br>8,100<br>500        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .19<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 220                                       | 47.                                           |
| OWEN,<br>Newark, NJ                | 40 03 24            | 82 24 24             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 300<br>8,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.26<br>.001     | 8,760<br>8,760<br>8,760 | 10                                        | 2.                                            |
| PPG,<br>Circleville,<br>OH         | 39 36 12            | 82 56 48             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 900<br>8,100<br>70           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .03<br>.26<br>.002     | 8,760<br>8,760<br>8,760 | 35                                        | 7.                                            |
| REICHHOLD,<br>Cateret, NJ          | 40 34 24            | 74 13 18             | 1    | Polyether<br>Polyols | P<br>E<br>S   | 500<br>8,100<br>40           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.         | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .02<br>.26<br>.001     | 8,760<br>8,760<br>8,760 | 20                                        | 4.                                            |

a Reference 7

TABLE 5.3.1-1 POLYETHER POLYOLS FOR URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE        | LATITUDE<br>(° ' "N) | LONGITUDE<br>(° ' "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DUKA.<br>(hrs)          | 1985<br>capa-<br>city<br>(mil.<br>of lbs) | 1986 est.<br>consump-<br>tion of<br>P.O.(gg) |
|-----------------------------------|----------------------|-----------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|-------------------------------------------|----------------------------------------------|
| TEXACO,<br>Austin,<br>TX          | 30 16 54             | 97 44 30              | 0    | Polyether<br>Polyols | P<br>E<br>S   | 1,300<br>8,100<br>100        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.26<br>.003     | 8,760<br>8,760<br>8,760 | 47                                        | 10.                                          |
| TEXACO,<br>Conroe,<br>TX          | 30 18 48             | 95 27 24              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,300<br>8,100<br>100        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.26<br>.003     | 8,760<br>8,760<br>8,760 | 47                                        | 10.                                          |
| TEXACO,<br>Port Neches,<br>TX     | 29 59 30             | 93 57 42              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,300<br>8,100<br>100        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.26<br>.003     | 8,760<br>8,760<br>8,760 | 47                                        | 10.                                          |
| STEPAN,<br>Millsdale,<br>IL       | 41 26 00             | 88 10 00              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 300<br>8,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.26<br>.001     | 8,760<br>8,760<br>8,760 | 8                                         | 2.                                           |
| UNION CARBIDE<br>Institute,<br>WV | 38 22 55             | 81 47 07              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 4,000<br>8,100<br>310        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .13<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 147                                       | 31.                                          |
| UNION CARBIDE<br>Seadrift,<br>TX  | 28 24 54             | 96 42 30              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 4,000<br>8,100<br>310        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .13<br>.26<br>.01      | 8,760<br>8,760<br>8,760 | 147                                       | 31                                           |

a Reference 7.

TABLE 5.3.1-1 POLYETHER POLYOLS FOR URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE                  | LATITUDE<br>(° ' "N) | LONGITUDE<br>(° ' "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE)<br>(g/s) | DURA.<br>(hrs)          | 1985<br>capa-<br>city <sup>a</sup><br>(mil.<br>of lbs) | 1986 est.<br>consump-<br>tion of<br>P.O.(Gg) |
|---------------------------------------------|----------------------|-----------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|-------------------------|-------------------------|--------------------------------------------------------|----------------------------------------------|
| UNION CARBIDE<br>South<br>Charleston,<br>WV | 38 22 00             | 81 44 00              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 4,000<br>8,100<br>310        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .13<br>.26<br>.01       | 8,760<br>8,760<br>8,760 | 147                                                    | 31.                                          |
| UPJOHN,<br>LaPorte, TX                      | 29 39 54             | 95 01 00              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>8,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.26<br>.001      | 8,760<br>8,760<br>8,760 | 15                                                     | 3.                                           |
| WITCO,<br>Chicago, IL                       | 41 53 00             | 87 37 30              | 1    | Polyether<br>Polyols | P<br>E<br>S   | 600<br>8,100<br>50           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .02<br>.26<br>.002      | 8,760<br>8,760<br>8,760 | 25                                                     | 5.                                           |

a Reference 7.

TABLE 5.3.1-2 POLYETHER POLYOLS FOR NON-URETHANE APPLICATIONS  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE   | LATITUDE<br>(° "N) | LONGITUDE<br>(° "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985 <sup>a</sup><br>capa-<br>city<br>(mt)<br>lbs | 1986<br>consump-<br>tion of<br>P.O.(Gg) |
|------------------------------|--------------------|---------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|---------------------------------------------------|-----------------------------------------|
| BASF,<br>Washington,<br>NJ   | 40 45 30           | 74 58 54            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>2,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.07<br>.001     | 8,760<br>8,760<br>8,760 | 20                                                | 3.2                                     |
| BASF,<br>Wyandotte,<br>MI    | 42 12 00           | 83 09 00            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,700<br>2,100<br>130        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .05<br>.07<br>.004     | 8,760<br>8,760<br>8,760 | 80                                                | 13                                      |
| DIAMOND,<br>Cedartown,<br>GA | 34 00 48           | 85 15 18            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                | 1.6                                     |
| DOW<br>Freeport,<br>TX       | 28 57 06           | 95 21 18            | 0    | Polyether<br>Polyols | P<br>E<br>S   | 1,000<br>2,100<br>80         | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .03<br>.07<br>.002     | 8,760<br>8,760<br>8,760 | 50                                                | 8.0                                     |
| HODAG,<br>Skokie, IL         | 42 02 36           | 87 44 48            | 0    | Polyetner<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                | 1.6                                     |
| ICI<br>New Castle,<br>DE     | 39 39 48           | 75 33 42            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                | 1.6                                     |

<sup>a</sup> Reference 7. Appendix C contains explanations of the fields in the table.

TABLE 5.3.1-2 POLYETHER POLYOLS FOR NON-URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| CUMAPNY,<br>CITY,<br>STATE           | LATITUDE<br>(° "N) | LONGITUDE<br>(° "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985 <sup>a</sup><br>capa-<br>city<br>(mtl<br>lbs) | 1986<br>consump-<br>tion of<br>P.O.(Gg) |
|--------------------------------------|--------------------|---------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|
| NALCO,<br>Carson, CA                 | 33 48 24           | 118 17 00           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>2,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.07<br>.001     | 8,760<br>8,760<br>8,760 | 20                                                 | 3.2                                     |
| NALCO,<br>Sugarland,<br>TX           | 29 37 06           | 95 37 48            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>2,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.07<br>.001     | 8,760<br>8,760<br>8,760 | 20                                                 | 3.2                                     |
| EMERY,<br>Mauldin,<br>SC             | 34 47 00           | 82 19 18            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                 | 1.6                                     |
| EMERY,<br>Santa Fe<br>Springs,<br>CA | 33 56 30           | 118 04 18           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>13.<br>6.           | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                 | 1.6                                     |
| OLIN,<br>Brandenburg,<br>KY          | 38 00 00           | 86 10 12            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 800<br>2,100<br>60           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .03<br>.07<br>.002     | 8,760<br>8,760<br>8,760 | 40                                                 | 6.4                                     |
| PELTON,<br>Lyons, IL                 | 41 48 36           | 87 49 30            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .007<br>.07<br>.0005   | 8,760<br>8,760<br>8,760 | 10                                                 | 1.6                                     |

a Reference 1.

TABLE 5.3.1-2 POLYETHER POLYOLS FOR NON-URETHANE APPLICATIONS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE                  | LATITUDE<br>(° "N) | LONGITUDE<br>(° "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985 <sup>a</sup><br>capa-<br>city<br>(mil<br>lbs) | 1986<br>consump-<br>tion of<br>P.O.(Gg) |
|---------------------------------------------|--------------------|---------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|
| UNION CARBIDE<br>Institute,<br>WV           | 38 22 55           | 81 47 07            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,400<br>2,100<br>110        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.07<br>.003     | 8,760<br>8,760<br>8,760 | 67                                                 | 11.                                     |
| UNION CARBIDE<br>Seadrift,<br>TX            | 28 24 54           | 96 42 30            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,400<br>2,100<br>110        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.07<br>.003     | 8,760<br>8,760<br>8,760 | 67                                                 | 11.                                     |
| UNION CARBIDE<br>South<br>Charleston,<br>WV | 38 22 00           | 81 44 00            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 1,400<br>2,100<br>110        | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .04<br>.07<br>.003     | 8,760<br>8,760<br>8,760 | 67                                                 | 11.                                     |
| WITCO,<br>Houston, TX                       | 29 45 48           | 95 21 42            | 0    | Polyether<br>Polyols | P<br>E<br>S   | 400<br>2,100<br>30           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .01<br>.07<br>.0009    | 8,760<br>8,760<br>8,760 | 18                                                 | 2.9                                     |
| MAGNA,<br>Dayton, TX                        | 30 02 48           | 95 21 41            | 1    | Polyether<br>Polyols | P<br>E<br>S   | 200<br>2,100<br>20           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .008<br>.07<br>.0006   | 8,760<br>8,760<br>8,760 | 12                                                 | 1.9                                     |
| MAGNA,<br>Houston, TX                       | 29 45 48           | 95 21 42            | 0    | Polyether<br>Polyols | P<br>E<br>S   | 100<br>2,100<br>10           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .004<br>.07<br>.0003   | 8,760<br>8,760<br>8,760 | 6                                                  | 1.0                                     |
| MAGNA,<br>Santa Fe<br>Springs,<br>CA        | 33 56 30           | 118 04 18           | 1    | Polyether<br>Polyols | P<br>E<br>S   | 100<br>2,100<br>10           | 200<br>2,000<br>-----     | 0<br>1<br>1  | 13.<br>3.<br>6.            | .03<br>-----<br>.03   | 1.1<br>.01<br>.01      | 300<br>300<br>300     | .004<br>.07<br>.0003   | 8,760<br>8,760<br>8,760 | 6                                                  | 1.0                                     |

a Reference 7.

### 5.3.2 Propylene Glycols

For facilities lacking explicit dipropylene glycol and tripropylene glycol capacity values, these values were assumed to be 10 percent and 1 percent, respectively, of the propylene glycol product.<sup>8</sup>

Table 5.3.2-1 lists capacities, consumption, and emissions for non-urethane polyether polyol facilities. Appendices D, E, F, and H contain calculations and assumptions made to obtain these values.

TABLE 5.3.2-1 PROPYLENE GLYCOL, DIPROPYLENE GLYCOL AND TRIPROPYLENE GLYCOL  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE                  | LATITUDE<br>(°' "N) | LONGITUDE<br>(°' "W) | ZONE | PROCESS<br>IDENT.    | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs)          | 1985 <sup>a</sup><br>Capa-<br>city<br>PG,DPG,<br>TPG<br>(ml<br>lbs) | 1986<br>est. •<br>con-<br>sump-<br>tion<br>(Gg) |
|---------------------------------------------|---------------------|----------------------|------|----------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|---------------------------------------------------------------------|-------------------------------------------------|
| ARCO,<br>Bayport, TX                        | 29 39 08            | 95 01 52             | 1    | Propylene<br>Glycols | P<br>E<br>S   | 1,700<br>16,800<br>600       | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>-----<br>.03   | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .06<br>.53<br>.02      | 8,760<br>8,760<br>8,760 | 272                                                                 | 62.                                             |
| DOW,<br>Freeport, TX                        | 28 57 06            | 95 21 18             | 0    | Propylene<br>Glycols | P<br>E<br>S   | 1,800<br>16,800<br>600       | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>-----<br>.03   | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .06<br>.53<br>.02      | 8,760<br>8,760<br>8,760 | 277                                                                 | 63.                                             |
| DOW<br>Plaquemine,<br>LA                    | 30 17 00            | 91 14 06             | 1    | Propylene<br>Glycols | P<br>E<br>S   | 1,100<br>16,800<br>400       | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>-----<br>.03   | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .03<br>.53<br>.01      | 8,760<br>8,760<br>8,760 | 167                                                                 | 38.                                             |
| OLIN,<br>Brandenburg,<br>KY                 | 38 00 00            | 86 10 12             | 1    | Propylene<br>Glycols | P<br>E<br>S   | 700<br>16,800<br>300         | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>-----<br>.03   | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .02<br>.53<br>.01      | 8,760<br>8,760<br>8,760 | 111                                                                 | 25.                                             |
| UNION CARBIDE<br>South<br>Charleston,<br>WV | 38 22 00            | 81 44 00             | 1    | Propylene<br>Glycols | P<br>E<br>S   | 600<br>16,800<br>200         | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>-----<br>.03   | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .02<br>.53<br>.01      | 8,760<br>8,760<br>8,760 | 87                                                                  | 20.                                             |

<sup>a</sup> Reference 4. Appendix C contains explanations of the field titles used in the table.

### 5.3.3. Glycol Ethers

To obtain emission estimates for this category, it was necessary to assume that the propylene glycol emission factors were applicable for this source category.<sup>9</sup>

Table 5.3.3-1 lists capacities, consumption, and emission data for this category.

TABLE 5.3.3-1 GLYCOL ETHERS  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE                | LATITUDE<br>(°' "N) | LONGITUDE<br>(°' "W) | ZONE | PROCESS<br>IDENT. | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DURA.<br>(hrs) | 1985 <sup>a</sup><br>Capa-<br>city<br>PG,DPG,<br>TPG<br>(mil<br>lbs) | 1986<br>est.<br>con-<br>sump-<br>tion<br>(Gg) |
|-------------------------------------------|---------------------|----------------------|------|-------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|----------------|----------------------------------------------------------------------|-----------------------------------------------|
| ARCO,<br>Channelview,<br>TX               | 29 45 30            | 95 07 30             | 1    | Glycol<br>Ethers  | P             | 50                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .002                   | 8,760          | 100                                                                  | 1.8                                           |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 20                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .001                   | 8,760          |                                                                      |                                               |
| DOW,<br>Midland, MI                       | 43 37 06            | 84 13 54             | 1    | Glycol<br>Ethers  | P             | 30                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .001                   | 8,760          | 55                                                                   | 0.98                                          |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 10                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .0003                  | 8,760          |                                                                      |                                               |
| DOW,<br>Plaquemine,<br>LA                 | 30 17 00            | 91 14 06             | 0    | Glycol<br>Ethers  | P             | 30                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .001                   | 8,760          | 60                                                                   | 1.1                                           |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 10                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .0003                  | 8,760          |                                                                      |                                               |
| ULIN,<br>Brandenburg,<br>KY               | 38 00 00            | 86 10 12             | 1    | Glycol<br>Ethers  | P             | 20                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .001                   | 8,760          | 45                                                                   | 0.80                                          |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 10                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .0003                  | 8,760          |                                                                      |                                               |
| UNION CARBIDE<br>Penuelas,<br>Puerto Rico | 18 03 36            | 66 43 06             | 1    | Glycol<br>Ethers  | P             | 40                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .001                   | 8,760          | 82                                                                   | 1.5                                           |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 20                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .0005                  | 8,760          |                                                                      |                                               |
| UNION CARBIDE<br>Seadrift, TX             | 28 24 54            | 96 42 30             | 1    | Glycol<br>Ethers  | P             | 40                           | 500                       | 0            | 27                         | .05                   | 3.3                    | 278                   | .001                   | 8,760          | 82                                                                   | 1.5                                           |
|                                           |                     |                      |      |                   | E             | 16,800                       | 45,000                    | 1            | 3                          | -----                 | .01                    | 300                   | .53                    | 8,760          |                                                                      |                                               |
|                                           |                     |                      |      |                   | S             | 20                           | -----                     | 1            | 6                          | .03                   | .01                    | 300                   | .0005                  | 8,760          |                                                                      |                                               |

a Reference 10. All capacities except that for ARCO were given for ethylene and propylene glycol ethers. It was assumed that propylene oxide based ethers comprised half of each facility's capacity.

TABLE 5.3.3-1 GLYCOL ETHERS (cont.)  
HEM INPUTS

| COMPANY,<br>CITY,<br>STATE | LATITUDE<br>(° ' "N) | LONGITUDE<br>(° ' "W) | ZONE | PROCESS<br>IDENT. | EMIS.<br>TYPE | ANN.<br>EMIS.<br>(kg/<br>yr) | AREA<br>(m <sup>2</sup> ) | VENT<br>TYPE | EMIS.<br>REL.<br>HT<br>(m) | STACK<br>DIAM.<br>(m) | EMIS.<br>VEL.<br>(m/s) | EMIS.<br>TEMP.<br>(K) | EMIS.<br>RATE<br>(g/s) | DUKA.<br>(hrs)          | 1985 <sup>a</sup><br>Capa-<br>city<br>PG,DPG,<br>TPG<br>(mil<br>lbs) | 1986<br>est.<br>con-<br>sump-<br>tion<br>(Gg) |
|----------------------------|----------------------|-----------------------|------|-------------------|---------------|------------------------------|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------------|------------------------|-------------------------|----------------------------------------------------------------------|-----------------------------------------------|
| UNION CARBIDE<br>Taft, LA  | 29 59 00             | 90 27 00              | 1    | Glycol<br>Ethers  | P<br>E<br>S   | 40<br>16,800<br>20           | 500<br>45,000<br>-----    | 0<br>1<br>1  | 27<br>3<br>6               | .05<br>----<br>.03    | 3.3<br>.01<br>.01      | 278<br>300<br>300     | .001<br>.53<br>.0005   | 8,760<br>8,760<br>8,760 | 82                                                                   | 1.5                                           |

<sup>a</sup> Reference 10. All capacities except that for ARCO were given for ethylene and propylene glycol ethers. It was assumed that propylene oxide based ethers comprised half of each facility's capacity.

#### 5.3.4 Miscellaneous

The propylene oxide emissions information was available which allowed short-term modeling data to be developed for the minor use of fumigation or sterilization. This minor use is one of the few direct uses of propylene oxide. In 1986, 170 Mg (380,000 lbs) of propylene oxide was used domestically for fumigation.<sup>12</sup>

##### 5.3.4.1. Site Specific Data

Direct use of propylene oxide includes a variety of categories. These uses were discovered through site specific data requests to state agencies. Propylene oxide is used as a solvent or stabilizer in paint mixtures. Propylene oxide also serves an unknown function in ski goggle assembly.<sup>13</sup> Because they consume so little of the chemical to begin with, it is likely that these types of facilities emit proportionately small quantities of propylene oxide. Emissions data were not available for these minor uses.

Propylene oxide is used in four unspecified facilities in Philadelphia which reportedly emit a total of 850 lbs of propylene oxide per year.<sup>14</sup> This amount is not significant relative to the facilities in the major use categories.

##### 5.3.4.2. Short-Term Data

For the direct use of propylene oxide as a fumigant or sterilant, the quantity of emissions, frequency of emissions, and general potential for exposure are areas of interest. The following data will help to quantify possible exposure due to use of propylene for these uses. The data below are extracted from data for a sterilization facility in Illinois.<sup>15</sup>

A sterilization facility uses six stacks for emissions from these retorts. Table 5.3.4-1 lists parameters which characterize the emission streams and the stacks.

TABLE 5.3.4-1 EMISSION PARAMETERS

|                 |      |
|-----------------|------|
| Height (m)      | 12.  |
| Diameter (m)    | 0.08 |
| Temperature (K) | 370. |
| Velocity (m/s)  | 16.  |

Propylene oxide comprises only 10 wt percent of the total annual gaseous fumigant usage. For the short-term calculations, it was assumed that pure propylene oxide was used simultaneously in the retorts.

The average sterilization cycle lasts 8 hours. The total emissions time during this cycle is 75 minutes. The emission time is not continuous. A break is necessary for the intake of air. The length of time of this break is unknown. For modeling purposes, the emission time was assumed continuous for 60 minutes.

The total amount of propylene oxide emitted in that hour is 170 kg. The emission rate is 47 g/s. Appendix I contains the details of the calculation.

Additional work was done to refine this emission estimate. These calculations and comments are given in Appendix J.

#### 5.4 REFERENCES

1. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Compilation of Air Pollution Emission Factors, 4th edition, Vol I, Stationary Point and Area Sources. Research Triangle Park, NC. September 1985. p.1.
2. Mannsville Chemical Products Corporation. Chemical Products Synopsis: Propylene Oxide. Cortland, NY. February 1984.
3. Chemical Imports in 1984. Chemical Week. February 20, 1985. p.36.
4. SRI International. 1985 Directory of Chemical Producers. Menlo Park, CA. 1985. p.550, 623, 827-830, 844, 950.
5. Ibid, p.844.
6. Ibid, p.550, 623, 827-830, 844, 950.
7. Ibid. p.829, 830.
8. SRI International, Chemical Economics Handbook. Menlo Park, CA. August 1980, p.690. 6050C.
9. Systems Applications, Inc. (SAI). Appendix A-25: Propylene Oxide. In: Human Exposure to Atmospheric Concentrations of Selected Chemicals, Vol II. Prepared for Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, NC. Contract No. 68-02-306. February 1982.
10. Reference 4. p.623.
11. Bogyo, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/11-80-005. March 1980. p.156.
12. Letter and attachments from M. Warren, ABERCO, Inc. to G. Hume, U.S. EPA, September 4, 1986. Fumigation with Propylene Oxide.
13. Information obtained through Air Pollution Control Office, New York State Department of Environmental Conservation, Albany, NY. 1986.
14. Lazenka, C.A., N.J. Ciciretti, R.T. Ostrowski, and W. Reilly. Experiences with Toxic Air Contaminant Control in Philadelphia. In: 76th Annual Meeting of the Air Pollution Control Association, Atlanta, GA. June 1983. Paper No. 83-46.3.
15. Information obtained through Air Pollution Control Division, Illinois Environmental Protection Agency, Springfield, Ill. 1986.

## 6. OTHER INFORMATION

### 6.1. AQUEOUS EMISSIONS

Generally, organic emissions are not transferred from air to water.<sup>1</sup> This might not be the case for propylene oxide because propylene oxide is water soluble and, at ambient conditions, it exists in the liquid phase.

Propylene oxide can be discharged from facilities into effluent water. This occurrence has been discovered at at least one facility.<sup>2</sup> Quantifying data were not available for this discharge.

Because propylene oxide is not completely soluble in water, and because it has a high vapor pressure, propylene oxide might evaporate from effluent emissions. This evaporation rate has been estimated to be approximately equal to the hydrolysis rate of propylene oxide.<sup>3</sup> Information on effluent streams was not available for any of the source categories. Therefore, estimates of secondary emissions were not made.

### 6.2. AMBIENT AIR CONCENTRATIONS

No literature was found in which propylene oxide had been measured in ambient air. This might be due to any of a number of factors. The most obvious explanation is that it might not be emitted in detectable quantities. Propylene oxide is highly reactive. This reactivity could prevent it from accumulating in measurable quantities. Rapid dispersion in areas where propylene oxide is emitted might also reduce the probability of measurement.

Propylene oxide is a volatile organic chemical which participates in the photochemical smog cycle.<sup>4,5</sup>

### 6.3. ENVIRONMENTAL FATE

Epoxides, such as propylene oxide, neither persist in the environment nor accumulate in the food chain. They are rarely identified in monitoring studies, but their degradation products have been identified.<sup>3</sup>

Epoxides are likely to migrate rapidly in soil. They have significant mobility in both water and air. This results from the combination of high water solubility and high vapor pressure.<sup>6</sup> Propylene oxide can degrade to a glycol or a halohydrin, or it can be biodegraded or evaporated from water.

In water, the evaporation rate is thought to be competitive with the hydrolyzation rate. Table 6.3-1 lists estimated half lives for propylene oxide degradation in water. The values in this table do not take biodegradation routes into account. An estimated 70 percent of propylene oxide biodegrades in 30 days in water.<sup>3,6</sup>

TABLE 6.3-1 PROPYLENE OXIDE DEGRADATION IN WATER <sup>a</sup>  
AT A TEMPERATURE OF 25°C

| pH                        | 5    | 7   | 9   |
|---------------------------|------|-----|-----|
| Half life (hrs)           |      |     |     |
| Fresh water               | 159  | 279 | 279 |
| Marine water              | 36.3 | 99  | 99  |
| <u>Chlorohydrin</u> ratio | 3-4  | 4.3 | 4.3 |
| <u>Glycol</u>             |      |     |     |

<sup>a</sup> Boggy, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. EPA-560/11-80-U05. March 1980. p. 84.

One reference estimated that in the atmosphere, the residence time for propylene oxide is 8.9 days. The residence time is not a concentration lifetime but the time required for a quantity of the pure chemical to be reduced to 1/e, approximately 0.37, of its original value.<sup>7</sup> Other atmospheric degradation pathways include free radical oxidation in reactions with ozone, O<sub>3</sub>, or the hydroxyl radical, •OH.<sup>9</sup> Table 6.3-2 lists possible atmospheric degradation products of propylene oxide.

TABLE 6.3-2 ATMOSPHERIC DEGRADATION PRODUCTS OF PROPYLENE OXIDE<sup>a,b,c</sup>

| <u>Name</u>          | <u>Chemical Formula</u>                            |
|----------------------|----------------------------------------------------|
| isopropyl alcohol    | CH <sub>3</sub> CHOHCH <sub>3</sub>                |
| n-propyl alcohol     | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH |
| propion aldehyde     | CH <sub>3</sub> CH <sub>2</sub> CHO                |
| acetone              | CH <sub>3</sub> COCH <sub>3</sub>                  |
| formaldehyde         | CH <sub>2</sub> O                                  |
| 2-oxo-propanal       | CH <sub>3</sub> COCHO                              |
| methyl ester acetate | CH <sub>3</sub> COOCHO                             |
| methanoic anhydride  | CHOCHO                                             |

a Cupitt, L.T. Fate of Toxic and Hazardous Materials in the Air Environment. Office of Research and Development. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-80-084. August 1980. p.19-21.

b Gritter, R.J. and E.C. Sabatino. Free Radical Chemistry of Cyclic Ethers. VII. Ultraviolet Photolysis of Epoxides and Propylene Sulfide in the Liquid Phase. Journal of Organic Chemistry. 29: 1966-1967. 1964.

c Nitrogen containing species are also possible degradation products.

#### 6.4. OCCUPATIONAL EXPOSURE DATA

In its 1985-1986 pamphlet, the American Conference of Governmental Industrial Hygienists (ACGIH) set a Threshold Limit Value-Time Weighted Average (TLV-TWA) of 20 ppm or 50 mg/m<sup>3</sup> for propylene oxide.

The people most likely to be exposed to this chemical are the process operators, maintenance personnel, tank car loaders and others who work with it directly. Exposure data which were readily available are given in tables 6.4-1, 2 and 3.

TABLE 6.4-1 MAXIMUM PEAK CONCENTRATIONS<sup>a,b</sup>

| <u>Activity</u>           | <u>Worst Case<br/>1979 (ppm)</u> | <u>Typical with<br/>Controls (ppm)</u> |
|---------------------------|----------------------------------|----------------------------------------|
| Process sampling          | 1,050                            | <1                                     |
| Tank car sampling         | 450                              | 1                                      |
| Tank car disconnect       | 150                              | -                                      |
| Gas chromatograph<br>work | 10                               | 4                                      |
| Other lab work            | 25                               | <1                                     |
| Maintenance               | 3,800                            | <1                                     |

<sup>a</sup> Exposure duration < 1 minute.

<sup>b</sup> Flores, G.H. Controlling Exposure to Alkene Oxides.  
Chemical Engineering Progress. 79:39-43. March 1983.

TABLE 6.4-2 TIME WEIGHTED AVERAGE EXPOSURE\*

|                  | <u>Typical daily<br/>exposure, 1979<br/>(ppm)</u> |
|------------------|---------------------------------------------------|
| Process operator | 2.0                                               |
| Tank car leader  | 2.0                                               |
| Maintenance      | 0.2                                               |

\*Flores, G.H. Controlling Exposure to Alkene Oxides.  
Chemical Engineering Progress. 79:39-43. March 1983.

TABLE 6.4-3 8-HOUR TIME WEIGHTED AVERAGE EXPOSURE, 1979\*

| <u>Activity</u>       | <u>High (ppm)</u> |             | <u>Low (ppm)</u> |             |
|-----------------------|-------------------|-------------|------------------|-------------|
|                       | <u>Dow</u>        | <u>ARCO</u> | <u>Dow</u>       | <u>ARCO</u> |
| Loading/drumming      | 8.5               | 9.5         | 2.4              | 1.1         |
| Process operator      | 2.4               | 1.1         | 1.3              | 0.1         |
| Maintenance           | 8.3               | -           | 2.8              | -           |
| Laboratory Technician | -                 | 10.6        | 1.0              | 0.7         |
| Tank farm operator    | -                 | 8.7         | -                | 0.8         |

\*Assessment of Testing Needs: Propylene Oxide, Support Document for Proposed Health Effects Test Rule. Office of Toxic Substances. U.S. Environmental Protection Agency, Washington, D.C.- 1983. p.16

## 6.5 REGULATIONS

At least three States--Connecticut, Nevada, and New York, have limits for the allowed concentration of propylene oxide in ambient air.<sup>11</sup> These limits are based upon health considerations, not upon monitoring data.

Some offices of the Federal Government have regulations concerning specific aspects of propylene oxide production and use.

The Department of Transportation (DOT) has issued various regulations concerning the labeling of containers and acceptable transportation vehicles (see Appendix F). The Occupation Safety and Health Administration (OSHA) has issued a permissible exposure level (PEL) for this chemical. To comply with this regulation may require the use of personal protective equipment, local exhaust ventilation, general dilution ventilation, and other measures.<sup>3,12</sup>

Within the Environmental Protection Agency (EPA), the Office of Pesticide Programs (OPP) regulates the amount of propylene oxide used for fumigation. This office can grant low volume (LV)-minor use waivers to allow this use. As has been discussed (see Section 3.4.4), the FDA also regulates the use of propylene oxide for fumigation of food.<sup>3,13</sup>

## 6.6 REFERENCES

1. Sittig, M., Environmental Sources Emissions Handbook. Prk Ridge, NJ. Noyes Data Corporation. 1975.
2. Schackelford, W. M. and L.H. Keith Frequency of Organic Compounds Identified in Water. Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA. EPA-600/4-76-062. December 1976. p.208.
3. Bogyo, D.A., S.S. Lande, W.M. Meylan, P.H. Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. EPA-560/11-80-005. March 1980. p.72, 73, 96, 150, 151.
4. Pitts, J.N., Jr., G.J. Doyle, A.C. Lloyd, and A.M. Winer. Chemical Transformations in Photochemical Smog and Their Applications to Air Pollution Control Strategies. National Science Foundation. National Technical Information Service (NTIS).
5. Akimoto, H., M. Hoshimo, G. Inoue, F. Sakamaki, H. Bandow, and M. Ukuda. Formation of Propylene Glycol 1,2-Dinitrate in the Photo-oxidation of a Propylene-Nitrogen Oxide-Air System. Journal of Environmental Science and Health. A/3(9):677-686. 1978.
6. Assessment of Testing Needs: Propylene Oxide, Support Document for Proposed Health Effects Test Rule. Office of Toxic Substances. U.S. Environmental Protection Agency, Washington, D.C. 1983. p.31
7. Cupitt, L.T. Fate of Toxic and Hazardous Materials in the Air Environment. Office of Research and Development. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-80-084. August 1980. p.19-21.
8. Gritter, R.J. and E.C. Sabatino. Free Radical Chemistry of Cyclic Ethers. VII. Ultraviolet Photolysis of Epoxides and Propylene Sulfide in the Liquid Phase. Journal of Organic Chemistry. 29:1965-1967. 1964.
9. Radding, S.B. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances. U.S. Environmental Protection Agency. Washington, D.C. EPA-560/5-75-001. January 1975. p.8.

10. Flores, G.H. Controlling Exposure to Alkene Oxides. Chemical Engineering Progress. 79:39-43. March 1983.
11. Information obtained through National Air Toxics Information Clearing House (NATICH) Data Base. September 1985. Office of Air Quality Planning and Standards. U.S. Environmental Protection Agency. Research Triangle Park, NC. EPA No. 68-02-3889, WA 25.
12. Occupational Health Guidelines for Propylene Oxide. National Institute for Occupational Safety and Health (NIOSH), U.S. Department of Health and Human Services, and Occupational Safety and Health Administration (OSHA), U.S. Department of Labor. September 1978.
13. The Food Chemical News Guide. Ford Chemical News, Inc. June 28, 1982. p.374.1-374.2

## Appendix A P.O. Production, Consumption, Import, Export

### Production<sup>1</sup>

1983 estimated P.O. production = 1,840 mil. lbs.

1983-1989 estimated growth rate = 4% per year.

$$(100 \frac{2.2 - 1.8}{1.8}) / 89-83 = 4\%$$

estimated production 1984 = (1,840) (1.04) = 1,900 mil. lbs.

1985 = 2,000 mil. lbs.

1986 = 2,100 mil. lbs.

### Imports

1. Imports are typically a minor share of total P.O. supply.<sup>2</sup>

2. Most imports come from Canada.<sup>3</sup>

3. In 1984, sizeable exports were made to Canada.<sup>4</sup>

Based upon these three facts, imports were assumed to be constant near their 1983, 1984 levels of 30 million lbs. per year.

### Exports

1980 total exports = 131 million lbs.<sup>5</sup>

1984 total exports = 180 million lbs.<sup>4</sup>

Annual Growth Rate:  $(\frac{180-131}{131}) / 84-80 = 9\%$

1985 estimated exports = (180) (1.09) = 200 mil. lbs.

1986 estimated exports = 210 mil. lbs.

### Consumption

Assuming the amount of P.O. in surplus or storage remains constant,

Production + Imports - Exports = Consumption

For 1986: 2,100 + 30 - 210 = 1,900 mil. lbs. (860 Gg)

1. Mannsville Chemical Products Corporation. Chemical Products Synopsis: Propylene Oxide. Cortland, New York, February 1984.
2. Assessment of Testing Needs: Propylene Oxide. Support Document for Proposed Health Effects Test Rule. Office of Toxic Substances. U.S. Environmental Protection Agency. Washington, D.C. 1983, p.8.
3. Bogyo, DA, SS Lande, WM Mcylan, PH Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA 560/11-80-005. March 1980. p. 15.
4. US Exports, Schedule B, Commodity by Country. Bureau of the Census, US Department of Commerce. Washington, D.C. FT 446. June 1985. p. 1-121.
5. US Exports, Schedule B, Commodity by Country. Bureau of the Census, US Department of Commerce. Washington, D.C. FT 446. April 1981. p. 1-138.

## Appendix B Production Facilities

### Utilization Factor:

$$\frac{2,100 \text{ mil lbs propylene oxide (PO) produced}}{2,870 \text{ mils lbs capacity}} = 73 \text{ percent utilization factor}$$

### Process Vent Emissions:

Process vent parameters were only available for two process vents of the chlorohydrination process. Since no other data were available, it was assumed that two process vents existed for both the chlorohydrination and the peroxidation processes and their parameters would be the same.

Table B - 1 - Process Vent Parameters<sup>1</sup>

|                | Height(m) | Diameter(m) | Temperature(K) | Velocity(m/s) |
|----------------|-----------|-------------|----------------|---------------|
| Reactor Vent   | 23.       | 0.30        | 289            | 1.5           |
| Condenser Vent | 14.       | 0.08        | 294            | 17.           |

### Chlorohydrin Vent Emissions:

Table B - 2 Chlorohydrination - Model Facility Vent Emissions<sup>2</sup>

| <u>Process Vent<sup>a</sup></u> | <u>Emission Source</u>   | <u>VOC Emissions<br/>(g/kg)<sup>b</sup></u> | <u>PO wt.% in VOC</u> | <u>PO Emission<br/>Factor(g/kg)<sup>c</sup></u> |
|---------------------------------|--------------------------|---------------------------------------------|-----------------------|-------------------------------------------------|
| Reactor Vent                    | Saponification<br>Column | .043                                        | 90.                   | .039                                            |
| Condenser Vent                  | PO Stripping             | .006                                        | 89.9                  | .016                                            |
|                                 | Light Stripping          | .006                                        | 79.9                  |                                                 |
|                                 | PO distillation          | .006                                        | 100.                  |                                                 |

<sup>a</sup> The stripping column and distillation emissions are all assumed to be emitted from the condenser vent because vent parameters were available only for one reaction vent and one condenser vent.

<sup>b</sup> g VOC emitted/kg PO produced

<sup>c</sup> PO emission factor for reactor vent = (VOC emissions)(PO wt %) =  
 $(.043)(.90) = 0.039 \text{ g/kg}$

condenser vent = (VOC emissions)(PO wt%)  
 $= .006(.899) + .006(.799) + .006(1.00) = .016 \text{ g/kg}$

Table B - 3 Emissions from Chlorohydrination Process Vents

| Company | Location       | Vent Type | Prod(Gg) | Emission Factor (g/kg) | Annual Emissions (kg/yr) <sup>a</sup> | Emission Rate (g/s) <sup>b</sup> |
|---------|----------------|-----------|----------|------------------------|---------------------------------------|----------------------------------|
| Dow     | Freeport, TX   | Reactor   | 310.     | 0.039                  | 12,200                                | .39                              |
|         |                | Condenser | 310.     | .016                   | 5,000                                 | .16                              |
|         | Plaquemine, LA | Reactor   | 130.     | .039                   | 5,200                                 | .16                              |
|         |                | Condenser | 130.     | .016                   | 2,100                                 | .07                              |

$$a. \text{ Annual Emissions} = (\text{Production})(\text{Emission Factor}) \left( \frac{1,000 \text{ kg/Gg}}{1 \text{ g/kg}} \right)$$

$$12,200 \text{ kg} = (310)(.039)(1,000)$$

$$b. \text{ Emission Rate} =$$

$$\frac{(n)/\text{kg}}{\text{yr}} \left| \frac{\text{yr}}{8,760} \right| \frac{\text{hr}}{3,600 \text{ s}} \left| \frac{1,000 \text{ g}}{\text{kg}} \right| = (n)(3.17 \times 10^{-5}) \text{ g/s}$$

$$(12,200)(3.17 \times 10^{-5}) = 0.39 \text{ g/s}$$

Peroxidation Vent Emissions:Table B - 4 Peroxidation - Model Facility Vent Emissions<sup>2</sup>

| Press Vent <sup>a</sup> | Emission Source <sup>b</sup>    | VOC Emissions (g/kg) <sup>bd</sup> | PO wt% in VOC <sup>b</sup> | PO Emission Factor (g/kg) |
|-------------------------|---------------------------------|------------------------------------|----------------------------|---------------------------|
| Reactor Vent            | PO Stripping                    | .0185                              | 100                        | .019                      |
| Condenser Vent          | Crude TBA Recovery <sup>c</sup> | .0155                              | trace                      | .0003                     |
|                         | Solvent Scrubber                | .63                                | 0.5                        |                           |

<sup>a</sup> The recovery and scrubber column emissions were assumed to be emitted from the condenser vent because vent parameters were only available for one reactor and one condenser vent.

<sup>b</sup> Ref. g. Separate tables were given in this reference for the isobutane and ethylbenzene peroxidation process. The values for ethylbenzene peroxidation yielded PO emission factors 100 times smaller than the total emission factors for isobutane peroxidation and chlorohydrination. It was assumed that the best estimate of PO emissions could be obtained by using the isobutane values for both peroxidation processes.

<sup>c</sup> Tertiary butyl alcohol = TBA

<sup>d</sup> g VOC emitted/kg PO produced

<sup>e</sup> Calculated in same manner as Table 7.2-2, footnote d.

Table B - 5 Emissions From Peroxidation Process Vents

| Company | Location        | Vent Type | Prod (Gg) | Emission Factor (g/kg) | Annual <sup>a</sup> Emissions (kg/yr) <sup>a</sup> | Emission <sup>a</sup> Rate (g/s) <sup>a</sup> |
|---------|-----------------|-----------|-----------|------------------------|----------------------------------------------------|-----------------------------------------------|
| Arco    | Bayport, TX     | Reactor   | 337       | .019                   | 6,400                                              | .20                                           |
|         |                 | Condenser | 337       | .003                   | 1,000                                              | .03                                           |
|         | Channelview, TX | Reactor   | 165       | .019                   | 3,100                                              | .10                                           |
|         |                 | Condenser | 165       | .003                   | 500                                                | .03                                           |

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<sup>a</sup> Calculated in same manner as corresponding columns in Table B-3.

## REFERENCES

1. Hydrosience, Incorporated. Trip Report to Dow in Plaquemine, LA. November 16-17, 1977. In: Hydrosience Files, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina
2. Peterson, CA (IT Enviroscience). Propylene Oxide Product Report. In: Organic Chemical Manufacturing Volume 10: Selected Processes. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA 450/3-80-028e. December 1980. p. IV-2, IV-6.

### Appendix C Comments Regarding HEM Input Tables

For all HEM Input tables, the following options apply:

- Zone - Urban = 0, rural = 1.  
Where the zone was unknown, it was assumed to be rural.
- Emission  
Type - Process vent = P, equipment leaks = E, storage = S  
Equipment leaks may also be referred to as fugitive emissions.
- Area - For vent or stack emissions = cross sectional downwash area,  
for equipment leaks = floor area. Where specific data was  
unavailable, these areas were based upon estimated dimensions of  
a manufacturing facility.
- Vent  
Type - Vertical = 0, nonvertical = 1  
Process vents were assumed to be vertical. All other vents and emissions  
were assumed non vertical.
- Duration - Continuous emissions = 24 hrs/day x 365 days/yr  
= 8,760
- Plant  
Location - The address given in Reference 10 was assumed correct for manufacturing  
facilities.
- Latitude,  
Longitude - The latitudes and longitudes given are those corresponding to the  
city name as listed in Reference 11. The precision of this Reference  
is 0.1 minutes (6 seconds). The accuracy of the values is a function  
of this precision and is dependent upon the actual location of the  
facility relative to the location of the city center. The following  
cities were not listed in Reference 11. Their angular measurements  
were obtained from various sources.

## REFERENCES

1. SRI International. 1985 Directory of Chemical Producers. Menlo Park, California, 1985. p. 550, 623, 827-830, 844, 950.
2. Gerlach, AC ed. The National Atlas of the United States of America. Geological Survey, U.S. Department of the Interior. Washington, D.C. 1970.

## Appendix D - Approximations of Stream Compositions

Notes from teleconference with West Virginia Environmental Protection Agency personnel, May 1, 1986.

Data in Table D-1 are from equipment leak estimates, Option #1 - Pump Seal Counts and Mass Balances for Union Carbide Corporation Facilities

Option #1 was one option used in developing the inventory for the state in which an average factor relating the number of equipment components per pump seal was used to derive total equipment counts based on multiplying the pump seal count for the process unit by this factor.

Table D-1 Stream Compositions

| Location                           | Process            | VOC(lb/yr) | PO(lb/yr) | Corresponding<br>Source<br>Category <sup>a,b</sup> | Wt. % POC |
|------------------------------------|--------------------|------------|-----------|----------------------------------------------------|-----------|
|                                    |                    |            |           |                                                    |           |
| South Charleston,<br>West Virginia | Flexible           | 47,200     | 1,660     | PP                                                 | 3.5       |
|                                    | Polyols            |            |           |                                                    |           |
|                                    | Phase 4            | 36,900     | 2,340     | PG                                                 | 6.4       |
|                                    | Ucon               |            |           |                                                    |           |
|                                    | Lubricants         | 116,000    | 3,850     | PP                                                 | 3.3       |
| Institute, WV                      | Flexible           | 73,800     | 12,600    | PP                                                 | 17.1      |
|                                    | Polyols            |            |           |                                                    |           |
|                                    | Rigid Polyols      | 18,000     | 1,130     | PP                                                 | 6.3       |
|                                    | Hydroxypropyl      | 828        | 738       | PG                                                 | 89.1      |
|                                    | Methisopropylamine | 1,180      | 499       | MI                                                 | 42.2      |
|                                    | Butoxyethoxy       | 384        | 325       | PG                                                 | 84.6      |
|                                    | Polyoxy            | 43,700     | 1,760     | MI                                                 | 4.0       |
| average for all streams            |                    |            |           |                                                    | 28.5      |

<sup>a</sup> PP - Polyether Polyols, PG - Propylene Glycol, MI - Miscellaneous

<sup>b</sup> This correspondence was assumed based upon product information for these facilities (see Table D-2).

<sup>c</sup>  $100 ((P.O. \text{ lb/yr}) / (VOC \text{ lb/yr})) = \text{wt\% P.O.}$

Appendix D - Approximations of Stream Compositions (cont'd)

Table D-2 Possible Products from Process Streams Propylene Oxide  
Products in South Charleston and Institute, WV

| <u>Location</u>      | <u>Products<sup>a</sup></u>                     |
|----------------------|-------------------------------------------------|
| South Charleston, WV | Polyether polyols for urethane applications     |
|                      | Polyether polyols for non-urethane applications |
|                      | Propylene Glycol                                |
|                      | Dipropylene Glycol                              |
|                      | Polypropylene Glycol                            |
|                      | n-Propoxypropanol                               |
| Institute, W Va      | Polyether polyols for urethane applications     |
|                      | Polyether polyols for non-urethane applications |
|                      | 1-Butoxyethoxy-2-propanol                       |

<sup>a</sup> SRI International. 1984 Directory of Chemical Producers, Menlo Park, California. 1984

Telecon. Dale Farley, West Virginia EPA, to G. Hume U.S. EPA on May 01, 1986. Propylene Stream Compositions at Industrial Consumption Sites.

## Appendix E Equipment Leaks

A correlation relating production rate to equipment leaks has not been found. Fluid vapor pressure, which is high for p.o., is a "primary factor influencing the equipment leak emission sources." <sup>1</sup> The complexity of a process unit influences the amount of equipment leak emissions. This complexity is indicated by the number of pump seals a facility has. Thus, the total equipment leak emissions of a specific VOC is a function of the number of pump seals in the facility. <sup>2</sup>

Table E-1 Baseline VOC Emissions<sup>a</sup>

|                                                                | A     | B      | C      |
|----------------------------------------------------------------|-------|--------|--------|
| Model Plant Pump Seals in<br>Light Liquid Service <sup>b</sup> | 8     | 29     | 91     |
| VOC Emissions (Mg/yr) <sup>c</sup>                             | 28.06 | 106.42 | 331.49 |

<sup>a</sup> "Baseline" means uncontrolled. A VOC is a volatile organic compound.

<sup>b</sup> Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. VOC Fugitive Emissions in Synthetic Organic-Chemicals Manufacturing Industry - Background Information for Promulgated Standards. Research Triangle Park, North Carolina. EPA 450/3-80-033b. June 1982. p.3-14.

<sup>c</sup> Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds-Additional Information on Emissions, Emission Reductions and Costs, EPA 450/3-82-010. April 1982. P B-3.

Table E-2 Emission Stream Parameters<sup>a</sup>

| Source<br>Category | Release<br>height (m) | Diameter<br>(m) | Temp<br>(K) | Velocity<br>(m/s) |
|--------------------|-----------------------|-----------------|-------------|-------------------|
| Production         | 3.0                   | 0.0             | 300         | 0.01              |
| Polyether polyols  | 3.0                   | 0.0             | 300         | 0.01              |
| Popylene glycols   | 3.0                   | 0.0             | 300         | 0.01              |

<sup>a</sup> Values given are default values which were used because specific information was not available.

### Production Facilities

For the p. o. production facilities, flow sheets of model plants were available. These flow sheets indicated that 31, 74 and 57 pumps were used at the chlorohydrin and peroxidation facilities.<sup>3</sup> All of these pumps were assumed to be in light liquid service. It was assumed that there was a spare in place for each pump located on the flow sheet. All production facilities were assumed to be of the same complexity. The best model for these plants was determined by averaging the number of pumps in the facilities.

$$\frac{2(31) + 2(74) + 2(57)}{3} = 108 \text{ average number of pumps}$$

The number of pumps corresponds to the number of pump seals. Model plant C, with 91 light liquid pump seals, was chosen as the best model for equipment leaks in p.o. production facilities.

To determine the amount of p.o. emissions, it was necessary to obtain an indication of the composition of the VOC streams. Available information indicated that 28.5 wt% would be a reasonable estimate. (see Appendix D).

Model C, VOC equipment leaks x wt % of PO = PO equipment leaks

$$(331.49 \text{ Mg/yr}) \times .285 = 94500 \text{ kg/yr}$$

$$\text{Emission rate} = (94500 \text{ kg/yr}) \left( 3.17 \times 10^{-5} \frac{\text{g/s}}{\text{kg/yr}} \right) = 3.00 \text{ g/s}$$

### Polyether Polyol

Process descriptions of polyether polyol urethane production were the basis for deciding that a model unit B was most appropriate for equipment leak estimates in urethane application.<sup>4,5</sup>

Because there is not a foaming process or urethane addition involved in non-urethane polyether polyol production, these non-urethane production units are believed to be less complex than the urethane processes. No data was available on which to base estimates of equipment leaks. Based upon a general understanding of process reactions and products, the model unit A facility was used to estimate equipment leaks for non-urethane production units.

A composition factor was determined using available data (see Appendix D). Based on information indicating production units at specific facilities (see Appendix D, table D-2), The following streams were assumed to be associated with the polyether polyol process units.

|                  |                    |
|------------------|--------------------|
| Flexible Polyols | 3.5 wt % PO in VOC |
| Flexible Polyols | 17.1               |
| Rigid Polyols    | 6.3                |
| Ucon Lubricants  | 3.3                |
| Avg.             | <u>7.6</u> wt %    |

(VOC emissions from Model Plant)(P.O. fraction) = PO emissions  
 Model Plant A: (28.06 Mg/yr)(.076) = 2.1 Mg/yr  
 Model Plant B: (106.42 Mg/yr)(.076) = 8.1 Mg/yr

#### Propylene Glycols and Glycol Ethers

Based upon a flow diagram and description of the hydration process, Model A was assumed to be the best model for equipment leaks from these processes.<sup>5</sup> Available data were used to determine stream composition (see Appendix D).

|                  |                 |
|------------------|-----------------|
| Phase 4          | 6.4 wt % PO/VOC |
| Hydroxypropylene | 89              |
| Butoxyethoxy     | 85              |
| Avg.             | <u>60</u> wt %  |

P.O. emissions = (28.06 Mg VOC/yr) (.60) = 16800 kg PO/yr

## REFERENCES

1. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds- Additional Information on Emissions, Emission Reductions and Costs, EPA 450/3-82-010. April 1982. P B-3.
2. Memorandum from Stelling, J. Radian to Evans, L.B., Office of Air Quality Planning and Standards, Environmental Protection Agency. April 15, 1986. Fugitive Emission Estimates - Kanawha Valley.
3. Peterson, CA (IT Envirosience). Propylene Oxide Product Report. In: Organic Chemical Manufacturing Volume 10: Selected Processes. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA 450/2-80-028e. December 1980. P. III-5,6,11-14,23-25. IV-2,6.
4. Mark, M.F., J.J. McKetta, D.F. Othmer, eds. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed. vol 21, John Wiley and Sons, New York. 1975. P 60-62, 80-94.
5. Considine, D.M. ed., Chemical and Process Technology Encyclopedia. McGraw-Hill Book Company. New York. 1974. 1121-1125.
6. Lowenheim, F.A. and M.K. Moran, Faith, Keyes, and Clark's Industrial Chemicals, 4th edition. John Wiley and Sons. New York. 1975.p.688,689.

## APPENDIX F - STORAGE AND TRANSPORTATION EMISSIONS

### Transportation

A primary consideration in the storage and transportation of propylene oxide (PO) is this compound's flammability. The high reactivity of PO is another important consideration.

The Department of Transportation (DOT) has developed regulations for this chemical.<sup>1</sup> PO may be transported by a variety of vehicles. It may be conveyed by ship or barge. Railroad tankers, holding 10,000 to 20,000 gallons, may be used. PO may also be transported in tank trucks or in 55 gallon drums.<sup>2</sup>

Emissions data were not available for any of these modes of transportation.

### Storage

The parameters in Table F-1 were used for storage emissions at all facilities. Storage emissions are not associated with an emission area.

Table F-1. Storage Emission Parameters<sup>a</sup>

| Height<br>(m) | Diameter<br>(m) | Velocity<br>(m/s) | Temperature<br>(K) |
|---------------|-----------------|-------------------|--------------------|
| 6.0           | 0.03            | 0.01              | 300                |

<sup>a</sup> Systems Applications, Inc. (SAI). Appendix A-26: Propylene Oxide. In: Human Exposure to Atmospheric Concentrations of Selected Chemicals. Vol. II. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. No. 68-02-306. February 1982.

### Storage at Production Facilities

The only data for storage emissions of PO indicated that a single fixed roof tank (height=45 feet, diameter=62 feet) at a production facility emitted 1 ton (1 Mg) of PO per year. It was implied that this was the only storage device used for PO. There was no indication of how frequently the tank was emptied and refilled.<sup>4</sup> A storage emission factor from another source<sup>3</sup> was used for the following calculations.

Table F-2. Storage Emissions at Production Facilities

| Company | Location              | Estimated<br>1986<br>Production<br>(Gg) | Annual PO<br>Storage Emissions <sup>a</sup><br>(kg) | Emission<br>Rate <sup>b</sup><br>(g/s) |
|---------|-----------------------|-----------------------------------------|-----------------------------------------------------|----------------------------------------|
| Arco    | Bayport, Texas        | 340                                     | 10,400                                              | 0.33                                   |
|         | Channelview, Texas    | 160                                     | 5,100                                               | 0.16                                   |
| Dow     | Freeport, Texas       | 310                                     | 9,700                                               | 0.31                                   |
|         | Plaquemine, Louisiana | 130                                     | 4,100                                               | 0.13                                   |

<sup>a</sup> Systems Applications, Inc. (SAI). Appendix A-26: Propylene Oxide. In: Human Exposure to Atmospheric Concentrations of Selected Chemicals. Vol. II. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. No. 68-02-306. February 1982.

<sup>b</sup> Emission factor=0.000031 lb P.O. emitted/lb P.O. produced.

#### Storage at User Sites

The only available source<sup>3</sup> gave an emission factor of .000001 lb PU emitted/lb of PO consumed. This number probably represents an assumed reasonable value rather than calculations from actual data.

Nothing in the available literature suggested that storage techniques or storage emission factors would vary greatly from production and user facilities. Since the emission factor used for production facilities was 0.000031 lb PU emitted/lb PU produced, it was considered more reasonable to use an estimated emission factor of 0.00001 lb PU emitted/lb PU consumed.

## STORAGE OF PROPYLENE OXIDE

Propylene oxide is a liquid under ambient conditions (20°C, 1atm). It has a low boiling point (34.2°C) and a high vapor pressure (445 mm Hg at 20°C). This means that it must be stored under pressure or in a manner which will minimize loss. Propylene oxide is also toxic and flammable. These characteristics encourage industrial consumers to minimize the amount of propylene oxide stored on the premises.

One example of storage of propylene oxide is given below. This example is considered typical for industry.<sup>5</sup>

The tanks used to store propylene oxide are blanketed with nitrogen. They are kept at a pressure slightly above atmospheric. The propylene oxide is kept cool by refrigerated vent condensers. Vapors emitted from the condensers go to a scrubber. Scrubber emissions are vented to a biological oxidation unit.

These storage tanks are on the premises of a propylene oxide production facility. The propylene oxide is pumped directly from the product distillation column. Most of the product is pumped from the tank directly to a propylene glycol production unit.

## REFERENCES

1. Grayson, M., ed. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition. Volume 19. New York, New York. John Wiley and Sons. 1982. p. 263.
2. Bogyo, DA, SS Lande, WM Mcylan, PH Howard, and J. Santodonato. Investigation of Selected Potential Environmental Contaminants: Epoxides. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA 560/11-80-005. March 1980. p. 62.
3. Systems Applications, Inc. (SAI). Appencix A-26: Propylene Oxide. In: Human Exposure to Atmospheric Concentrations of Selected Chemicals. Vol. II. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. No. 68-02-306. February 1982.
4. Hydrosience, Incorporated. Trip Report to Dow in Plaquemine, LA. November 16-17, 1977. In: Hydrosience Files, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina.
5. Telecon. G. Hume, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, to Mike Nevill, Dow Chemical. July 24, 1986. Propylene Oxide Storage File 86/22.

# APPENDIX G - CONSUMPTION ESTIMATES FOR USE CATEGORIES

The estimation of current consumption of PO was complicated by the fact that different references list different categories of use. It is not always clear which of these categories refer to the same use.

Table G-1 PO Usage<sup>a</sup>

|                                   | <u>1983</u><br><u>(% of consumption)</u> | <u>1985<sup>b</sup></u><br><u>(% of consumption)</u> |
|-----------------------------------|------------------------------------------|------------------------------------------------------|
| Polyurethane                      | 40                                       | 41                                                   |
| Flexible Foams                    | 7                                        | 7                                                    |
| Rigid Foams                       | 10                                       | 11                                                   |
| Noncellular                       | 7                                        | 6                                                    |
| Coatings and Adhesives            | 4                                        | 4                                                    |
| Polyols for Specialty Surfactants | 22                                       | 22                                                   |
| Propylene Glycol                  | 4                                        | 4                                                    |
| Detergents                        | 6                                        | 5                                                    |
| Other                             |                                          |                                                      |

<sup>a</sup>Mannsville Chemical Products Corporation. Chemical Products Synopsis:

Propylene Oxide. Cortland, New York, February 1984.

<sup>b</sup>Estimates made using 1983 estimates and growth predictions from Reference 1.

Table G-2. PO Usage\*

|                      | <u>1978</u><br><u>(% of consumption)</u> | <u>1983</u><br><u>(% of consumption)</u> |
|----------------------|------------------------------------------|------------------------------------------|
| Polyurethane Polyols | 62                                       | 64                                       |
| Flexible Foams       | (71)                                     |                                          |
| Rigid Foams          | (9)                                      |                                          |
| Non-Foam             | (10)                                     |                                          |
| Export               | (10)                                     |                                          |
| Propylene Glycol     | 21                                       | 21                                       |
| Dipropylene Glycol   | 3                                        | 3                                        |
| Glycol Ethers        | 1                                        | 1                                        |
| Miscellaneous        | 12                                       | 11                                       |

\*SRI International Chemical Economics Handbook, Menlo Park, California.  
1978-1980. p.690. 8021C,690.8022K.

The reference lists were reorganized into the desired categories.  
 From this information, the current use categories were estimated.

Table G-3. PO Consumption Estimates

|                                                      | <u>1983</u><br><u>(% of consumption)</u> | <u>1985</u><br><u>(% of consumption)</u> | <u>1986</u><br><u>(% of consumption)</u> |
|------------------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| Polyether Polyols<br>for Urethane<br>Applications    | 57                                       | 59                                       | 56                                       |
| Polyether Polyols<br>for Nonurethane<br>Applications | 7                                        | 12                                       | 11                                       |
| Propylene Glycols                                    | 24                                       | 22                                       | 24                                       |
| Glycol Ethers                                        | 1                                        | --                                       | 1                                        |
| Miscellaneous                                        | 11                                       | 7                                        | 8                                        |

REFERENCE G

1. Mannsville Chemical Products Corporation. Chemical Products Synopsis: Propylene Oxide. Cortland, New York, February 1984.
2. SRI International. Chemical Economics Handbook. Menlo Park, California. 1978-1980. p.690.8021C, 690.8022K.

# APPENDIX H - PROCESS VENT PARAMETERS

Table H-1 Process Vent Parameters<sup>a</sup>

| Source               | Release<br>Height<br>(m) | Diameter<br>(m) | Temperature<br>(K) | Velocity<br>(m/s) | Emission<br>Factor <sup>b</sup> |
|----------------------|--------------------------|-----------------|--------------------|-------------------|---------------------------------|
| Polyether<br>Polyols | 13                       | 0.03            | 300                | 1.1               | .00013                          |
| Propylene<br>Glycols | 27                       | 0.05            | 278                | 3.3               | .000028                         |

<sup>a</sup> Systems Applications, Inc. (SAI). Appendix A-26: Propylene Oxide.  
In: Human Exposure to Atmospheric Concentrations of Selected Chemicals.  
Vol. II. Office of Air Quality Planning and Standards, U.S. Environ-  
mental Protection Agency. Research Triangle Park, North Carolina.  
No. 68-02-306. February 1982.

<sup>b</sup> Lb PU emitted/lb PU consumed

# APPENDIX I - SHORT TERM EMISSIONS DATA

The following information was obtained for a sterilization facility.<sup>1</sup>

In 1984, the facility reported using 18,326 pounds (8,000 kg) of PO. This was 10 percent by weight of the total gaseous sterilants. The example situation desired for the emissions estimate was the use of 100 percent PO. Although the facility has six separate retorts, the emissions calculations were made assuming simultaneous emissions, which is calculated in the same way as assuming a single retort.

Table I-1. Emission Parameters

|                            |                            |
|----------------------------|----------------------------|
| Release Height (m)         | 12                         |
| Vent Diameter (m)          | .08                        |
| Emission Velocity (m/s)    | 16                         |
| Temperature (K)            | 370                        |
| Event Duration (min/cycle) | 75                         |
| Average Events/Day         | 1.5                        |
| Operating Hours            | 52 weeks/year, 5 days/week |

Total Emissions Per Event:

$$\frac{18,326 \text{ lbs PO/yr}}{.10 \text{ fraction of sterilants}} \times \frac{\text{year}}{52 \text{ weeks}} \times \frac{\text{week}}{5 \text{ days}} \times \frac{\text{day}}{1.5 \text{ events}} = 469.9 \text{ lb PO/event}$$

Emission Rate:

$$\frac{213 \text{ kg PO}}{\text{event}} \times \frac{\text{event}}{75 \text{ minutes}} \times \frac{1,000 \text{ g}}{\text{kg}} \times \frac{1 \text{ minute}}{60 \text{ seconds}} = 47 \text{ g/s}$$

For modeling purposes, total emissions for a 1 hour time period were calculated.

$$\frac{47 \text{ g}}{\text{s}} \times \frac{3,600 \text{ s}}{\text{hr}} \times \frac{\text{kg}}{1,000 \text{ g}} = 170 \text{ kg/hr}$$

## J. SHORT-TERM EMISSIONS ESTIMATES

Additional information was sought to recheck the assumptions which were used to calculate short-term emission rates. The information used for these emission estimates came from permit applications filed with the Illinois Environmental Protection Agency.<sup>1</sup> The permits were granted for the Micro-Biotrol, Incorporated sterilization facility in Willowbrook, Illinois. The additional information obtained<sup>2</sup> clarified facility operations and the methods of calculation which were given in the permit applications.

Two methods of calculation for short-term emission rates were used. The first method used past annual consumption to estimate current consumption. The annual consumption was converted to peak hourly rates using facility operation information contained in the permits. The second method used an average quantity of propylene oxide consumed per cycle to determine the peak hourly emissions. The peak emission rates obtained from these methods were both 0.2 Mg/hr.

The methods of calculation are given in Sections J.2 and J.3. Section J.1.1 contains general information about the use of propylene oxide as a fumigant.

### J.1 Propylene Oxide Fumigation

Every year, a small amount of propylene oxide is used as a fumigant. Regulations concerning this use are promulgated by the Food and Drug Administration (FDA). These regulations restrict the products on which propylene oxide may be used, limit the amount of residue, and set forth process restrictions. Propylene oxide may be used to fumigate dried prunes, glace fruit, cocoa, gums, spices, starch, and processed nut meats (except peanuts). The regulations establish acceptable residue levels of propylene oxide or of its reaction products propylene glycol or propylene chlorohydrin.<sup>3</sup>

Industry sources indicate that propylene oxide is used primarily to fumigate cocoa powder and shelled walnuts, almonds, and pecans.<sup>4,5</sup> Propylene oxide disinfests and destroys microorganisms in these foods. It is the only

effective and allowed fumigant for these processed nuts and cocoa powder.<sup>5</sup> Other fumigants may be used on nuts before they are shelled.

Methyl bromide has been used for disinfestation but it is not as effective against microorganisms.<sup>4</sup> Propylene oxide is superior to ethylene oxide on these foods for a number of reasons. Ethylene oxide can react with chemicals in the foods and degrade the quality of that product. This is the case with cocoa powder. Ethylene oxide would be a more effective fumigant because it is a more effective antimicrobial agent. However, it is also more toxic to humans, which means allowed residue would be smaller and worker contact would be a greater concern. Propylene oxide is less reactive with salts so it is less likely to form chlorohydrin than is ethylene oxide. Finally, both of these oxides can react to form their glycols. Ethylene glycol is toxic but propylene glycol is a chemical which is classified as Generally Recognized As Safe (GRAS) by the FDA.<sup>6</sup>

Two companies sell propylene oxide for fumigant uses. These companies are Union Carbide Corporation and ABERCO, Incorporated. They sold a combined total of 170 Mg (380,000 lbs) of propylene oxide for fumigation in 1986.<sup>5,7</sup> Propylene oxide demand for this consumption category is expected to increase because of increased demand for nuts in breakfast cereals.<sup>4</sup>

Propylene oxide is a liquid at ambient conditions. Its boiling point at atmospheric pressure is 34°C (94°F). To be used as a fumigant it must be in the vapor phase. This is accomplished by using vacuum chambers or by heating the fumigant or by doing both of these things. Applying too much heat to the system could cause product degradation.

For fumigation, propylene oxide is usually used in its 99.9 percent pure form. It can also be used in an 8 percent propylene oxide mixture with carbon dioxide. The mixture is generally not as effective as pure propylene oxide.<sup>4</sup>

During the process, the product usually sits in the fumigant for two to four hours at a temperature of 50°C (120°F).<sup>11</sup> After this time the sterilization chamber is evacuated to the atmosphere. If the facility uses ethylene oxide and if this fumigant is emitted from the same point as

the propylene oxide, there might be an air pollution control device for the ethylene oxide. This might also reduce propylene oxide emissions. One such control device is the scrubbing unit which has been installed at the fumigation facility in Willowbrook, Illinois.<sup>2,13</sup>

This scrubbing unit has a removal efficiency of 99.8 to 99.99 percent for ethylene oxide. It has an efficiency of 98 to 99 percent for propylene oxide. If desired, the system removal efficiency for propylene oxide could be increased. This would simultaneously increase the efficiency for ethylene oxide.<sup>8</sup>

Emission rates from ethylene oxide sterilization chambers have been modeled. The rate is an exponentially decaying function of the chamber volume, mass flow rate and time. The modeling indicates that 80 percent of the sterilant is emitted during the first 10 minutes of the emission phase.<sup>9</sup> It is reasonable to assume that propylene oxide emission rate is an exponentially decaying function. To obtain accurate peak emission rates for a shorter time period than the 1-hour basis used, it would be necessary to have more detailed information about process cycles and the timing of emission phases of different sterilization chambers.

Most propylene oxide fumigation facilities consume between 3 and 5 Mg (6,000 to 12,000 lbs) of propylene oxide annually. Industry sources indicated that the contract sterilization facility in Willowbrook, Illinois, is the largest single consumer for this use. This facility consumes 10 Mg (20,000 lbs) of propylene oxide annually. Industry sources felt that specific locations of propylene oxide fumigation facilities is confidential information. Some locations were assumed for modeling purposes (see Table 8.1). Since the Micro-Biotrol facility has the largest annual consumption, it was assumed that a peak hourly rate of emissions for that facility would be a reasonable peak hourly rate for the other facilities.<sup>4,6,7</sup>

TABLE J-1 PROPYLENE OXIDE FUMIGATION

| <u>Location<br/>State</u> | <u>City<sup>a</sup></u>  | <u>Percent Annual<br/>Fumigation Consumption<sup>d</sup></u> | <u>Annual Consumption<sup>e</sup><br/>(Mg/yr)</u> |
|---------------------------|--------------------------|--------------------------------------------------------------|---------------------------------------------------|
| California                | Fresno                   |                                                              | 20                                                |
|                           | Los Angeles              |                                                              | 20                                                |
|                           | Total                    | 35                                                           |                                                   |
| Georgia                   | Albany                   |                                                              | 4                                                 |
|                           | Total                    | 2.5                                                          |                                                   |
| Illinois                  | Chicago                  |                                                              | 17                                                |
|                           | Willowbrook <sup>b</sup> |                                                              | 9                                                 |
|                           | Total                    | 15                                                           |                                                   |
| New Jersey                | Boundbrook <sup>c</sup>  |                                                              | 6                                                 |
|                           | Newark                   |                                                              | 65                                                |
|                           | Union <sup>c</sup>       |                                                              | 6                                                 |
|                           | Total                    | 45                                                           |                                                   |
| Pennsylvania              | Hershey                  | 2.5                                                          | 4                                                 |
|                           | Total                    |                                                              |                                                   |

<sup>a</sup>The locations of fumigation facilities in the given cities were assumed unless otherwise noted. These general locations were checked with regional and State agencies. Reference 12.

<sup>b</sup>Reference 1

<sup>c</sup>Industry sources

<sup>d</sup>Reference 5

<sup>e</sup> (1) Percent consumption by State x total consumption = annual consumption by State.

(2)  $\frac{\text{annual consumption by State} - \text{known facility consumption}}{\text{city consumption assumed number of city locations}} = \text{estimated}$

## J.2 Annual Consumption Method

This method was used for the emission estimate given in Section 7.9 of this document.<sup>10</sup> The method is repeated in this section in more detail to explicate the calculations, data, and assumptions.

The company uses three gases for sterilization. In 1984, the facility consumed 100,000 lbs of ethylene oxide, 18,000 lbs. of propylene oxide, and 62,000 lbs of 12/88 (Freon). Ethylene oxide is used in pure form or in a mixture with Freon. Propylene oxide is used only in the pure form. Propylene oxide comprises 5 percent of the annual usage of gaseous sterilants.

The annual percentage gives no indication of the maximum number of retorts that may be using propylene oxide at a particular time. There are eight retorts at the facility. In order to calculate the maximum amount of p.o. emissions it was assumed that, at some time, propylene oxide could be in use in all of the retorts.

It was also assumed that all eight retorts could be in the emission stages of their cycles simultaneously. The average cycle length is 8 hours. During the cycle emissions occur in two phases. These phases average 45 minutes and 30 minutes for a total emission time of 1.25 hours. They are separated by an unspecified amount of time while the retort is filled with air up to atmospheric pressure. The amount of time necessary for the air influx would probably be minimal. Therefore, the short-term modeling could be based upon a single continuous one hour emission period.

In the original calculations for short-term emissions,<sup>10</sup> it was assumed that the same amount of p.o. would be consumed in 1986 as was consumed in 1984.

Because of the limits upon the amount of residue allowed on the food, it is desirable to evacuate as much fumigant as possible from the retort. It was assumed that all of the propylene oxide consumed would be emitted to the atmosphere from the retort.

An emission control device, a Best Available Control Technology (BACT) Deox unit, began operation in November 1987.<sup>13</sup> This start up date was rescheduled from January 1987 due to construction delays. The de-ox unit converts oxides into glycols. The control device is being installed primarily to reduce ethylene oxide emissions but it will also reduce propylene oxide emissions.<sup>8</sup>

## 1986 Emission Estimates

Average use of propylene oxide per cycle per retort --

18326 lb/yr      annual consumption<sup>1</sup>

$$\frac{18326 \text{ lb}}{\text{yr}} \times \frac{1 \text{ yr}}{52 \text{ wk}} \times \frac{1 \text{ wk}}{5 \text{ d}} \times \frac{1 \text{ d}}{12 \text{ hrs}^*} \times \frac{8 \text{ hrs}^*}{1 \text{ cycle}} = 47. \text{ lb po used/ cycle}^* (26. \text{ kg})$$

$$\frac{47 \text{ lb po/cycle}}{8 \text{ retorts}} = 5.9 \text{ lb po/cycle per retort} \\ (2.7 \text{ kg po/cycle per retort})$$

2.7 kg po consumed = 2.7 kg po emitted

$$\frac{2.7 \text{ kg po}}{\text{cycle}} \times \frac{100\% \text{ possible usage per cycle}}{10\% \text{ average usage per cycle}} \times \frac{1 \text{ kg emitted}}{1 \text{ kg used}} = 27 \text{ kg po/cycle} \\ \text{per retort emitted}$$

Eight retorts are assumed to emit simultaneously.

$$\frac{27 \text{ kg po/cycle}}{\text{retort}} \times 8 \text{ retorts} = 210 \text{ kg po emitted/cycle (564 lb po/cycle)}$$

Emission rates --

$$\frac{210 \text{ kg po}}{\text{cycle}} \times \frac{1 \text{ cycle}}{75 \text{ min}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ min}}{60 \text{ s}} = 47 \text{ g/s}$$

$$\frac{47 \text{ g}}{\text{s}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{3600 \text{ s}}{1 \text{ hr}} = 170 \text{ kg/hr}$$

\* Given or calculated as an average.

### J.3 Consumption Per Cycle Method

The second method for the calculation of propylene oxide emission rate is based upon the value that Micro-Biotrol, Inc, gave for the average amount of p.o. used per cycle.<sup>2</sup> Micro-Biotrol estimated that an average of 154 lbs (70 kg) of propylene oxide were consumed per cycle per retort. It was assumed that all of the propylene oxide consumed would be emitted. Assumptions regarding the length of time of the emissions during the average cycle were the same as those given in the previous section.

154. lb avg po used per cycle (70 kg)  
75 min avg evacuation time per cycle

For a single retort -

$$\frac{70 \text{ kg p.o.}}{\text{cycle}} \times \frac{\text{cycle}}{75 \text{ min}} = 0.93 \text{ kg/min}$$

$$0.93 \text{ kg/min} = 16 \text{ g/s} = 56 \text{ kg/hr}$$

Table J-2 Propylene Oxide Emissions

| Number of retorts emitting<br>p.o. simultaneously | emission rate<br>(g/s) | emissions per hour<br>(kg) |
|---------------------------------------------------|------------------------|----------------------------|
| 1                                                 | 16                     | 56                         |
| 2                                                 | 32                     | 110                        |
| 4                                                 | 62                     | 220                        |

Four retorts would be the maximum number emitting simultaneously.<sup>2</sup> It was assumed that all of these retorts would be using propylene oxide.

## References

1. Information obtained through Air Pollution Control Division, Illinois Environmental Protection Agency, Springfield, Illinois, permit I.D. No. 043110AAC, November 15, 1985.
2. Telcon. G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency to J. Kjellstrand, Micro-Biotrol, Inc. July 22, 1986 and July 28, 1986. Sterilization with Propylene Oxide. File 86/22.
3. Food Chemical News, Inc., The Food Chemical News Guide, June 28, 1982. p. 374.1, 374.2
4. Telcon. G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency to F. Mosebar, Dried Fruit Association of California. August 15, 1986. Fumigation with Propylene Oxide. File 86/22.
5. Letter and attachments from M. Warren, ABERCO, Inc. to G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency. September 4, 1986. Fumigation with Propylene Oxide.
6. Telcon. G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency to M. Warren, ABERCO, Inc. August 26, 1986. Fumigation with Propylene Oxide. File 86/22.
7. Telcon. G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency to C. Woltz, Union Carbide Corporation. November 16, 1986. Fumigation with Propylene Oxide. File 86/22.
8. Telcon. G. Hume, Emission Standards and Engineering Division, Environmental Protection Agency to T. Bonicor, Chemrox. August 26, 1986. Deox unit removal of Propylene Oxide. File 86/22.
9. Memorandum from D.L. Newton, Midwest Research Institute, to D.W. Markwords, Emission Standards and Engineering Division, Environmental Protection Agency. April 28, 1986. Short Term Emission Parameters for EU Sterilization Facilities.
10. See Section 5.3.4.2 and Appendix 7.9 of this report; i.e., G. Hume, Propylene Oxide: Preliminary Source Assessment. Environmental Protection Agency, Research Triangle Park, N.C., July 1986.
11. Letter and attachments from M. Warren, ABERCO, Inc. to National Toxicology Program, Research Triangle Park, N.C. November 3, 1986. Fumigation and Sterilization with Propylene Oxide.
12. Personnel Communication with N. Pate, Strategies and Air Standards Division, Environmental Protection Agency.
13. Telcon. G. Hume, Emission Standards Division, Environmental Protection Agency to Jim Cobb, permit section, Illinois Environmental Protection Agency. May 10, 1988. Deox unit at Microbiotrol Facility. File 86/22.